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DEVELOPMENT OF METHODS FOR THE STABILIZATION OF PYROLYTIC OILS

by

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Grant Numbers R-804440010 and R-804440020

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16. ABSTRACT

Capillary gas chromatographic, liquid chromatographic and coupled gas/mass spectrometric analysis procedures were developed to analyze pyrolytic oils produced from cellulosic waste residues. Some of the major components indentified were: ethanol, 1-butnaol; acetaldehyde; furfuryl alcohol; 5-methoylfurfural; and 4-hydroxy-3-methoxystyrene. The pyrolytic oils contained a number of valuable chemicals. Further investigations on the isolation of these valuable chemicals from pyrolytic oils are recommended.

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FOREWORD

The U. S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report describes developed capillary gas chromatographic, liquid chromatographic and coupled gas chromatographic/mass spectrometric analysis procedures for determining the chemical composition of pyrolytic oils.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

We have developed capillary gas chromatographic, liquid chromatographic and coupled gas chromatographic mass spectrometric analysis procedures for the pyrolytic oils. We have identified the major components of the oils and the chemical processes occurring. We have also initiated stabilization studies.

The major components identified were: ethanol; 1-butanol; isobutanol; acetaldehyde; furfuryl alcohol; 5-methylfurfural; 2-octanol; phenol; Guaiacol; m- and p-methoxyphenol; o-m- and p-cresoles; Veratrole; isobutyric acid; buryric acid; naphthalene; Estragole; Anethole; Eugenol; 2-methoxy-4-methylphenol; 2-methoxy-4-ethylphenol; 2-methoxy-4-propylphenol; Isoeugenol; dimethylphenols; hydroquinone; 2-hydrosy-5-methoxybenzaldehyde; 2-hydroxy-acethophenone, and 4-hydroxy-3-methoxystyrene.

Included among the chemical processes occurring over a period to time are the formation of acetals thorugh the reaction of aldehydes and alcohols, and the formation of esters through the reaction of acids and alcohols. We have also demonstrated that under the low pH conditions of the pyrolytic oils, Isoeugenol polymerizes readily. Other components which might polymerize under the conditions include Eugenol, Anethole, Estragole and 4-hydroxy-3-methoxystyrene.

We have hydrogenated afresh sample of pyrolytic oil in an attempt to stabilize the oil against polymerization. Hydrogenation of the oil resulted principally in the conversion of Isoeugenol and Eugenol to 2-methoxy-4-propylphenol, and 4-hydroxy-3-methoxystyrene to 2-methoxy-4-ethylphenol.

Utilizing aging studies, we have demonstrated that the disappearance of Isoeugenol, 4-hydroxy-3-methoxystyrene, and other polymerizable olefins corresponds to the increases in viscosities of the oil. We therefore propose a cationic chain-reaction polymerization mechanism for the increases in viscosity of the pyrolytic oils.

This report was submitted infulfillment of Grant Nos. R-804440010 and R-804440020 by the Atlanta University under the sponsorship of the U. S. Environmental Protection Agency. The report covers the period June 20, 1976 to May 31, 1980, and work was completed as of May 31, 1980.

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SECTION 1

INTRODUCTION

Every year, large amounts of agricultural waste are produced in the United States. The disposal of this waste material is becoming an increasingly more difficult and expensive matter. Also there is a critical need for new energy sources in the United States. Agricultural wastes are largely lignocellulosic in chemical nature. Pyrolysis is an excellent approach for the conversion of agricultural and wood manufacturing wastes to useful energy or chemical forms.

The products resulting from the pyrolysis of the organic fraction of solid wastes include noncondensable gases, liquids, and a solid residue of carbonaceous material or char.[1] Analysis of the evolved pyrolytic gas stream indicates the presence of hydrogen, carbon dioxide, carbon monoxide, methane, ethane, and ethylene. The individual gas compositions vary with pyrolysis conditions. The solid material which remains after pyrolysis is an impure carbon and ash. The liquid fraction or pyrolytic oil contains organics and water.

Workers at the Engineering Experiment Station at the Georgia Institute of Technology have shown that pyrolysis is readily utilized for the conversion of cellulosic and lignocellulosic wastes into useful fuels and other products. A large prototype pilot pyrolysis system constructed in 1972 [2] was built to operate continuously at an input feed rate of 300 to 500 lbs. of waste per hour. The system includes a waste receiving bin, a belt conveyor to the converter, the converter and char handling system, an off-gas cyclone, a condenser and a gas burner. Peanut shells, wood chips, pine bark and sawdust, municipal wastes, macadamia nut hulls and cotton gin wastes have been pyrolyzed in the pilot plant. A large 50-ton/day demonstration plant which is owned and operated by the Tech-Air Corporation is located in a wood yard in Cordele, Georgia and is operated on wastes from the sawmill.

The pyrolytic oils are mixtures of neutral compounds and strong and weak acids with pH's of 3-4. The oils are viscous, sticky liquids at room temperature. The pyrolytic oils appear to oxidize and/or polymerize on standing.

Many investigators have determined the products of the pyrolysis and distillation of wood. Some of the products identified are: Naphthalene; dimethylnaphthalene; 2,3-dimethylanthracene; 2-methoxy-4-methylphenol; Guaiacol; 2-methoxy-4-ethylphenol; 2-methoxy-4-propylphenol;

phenol; cresols; xylenols; pyrocatechol; 4-methylpyrocatechol; dimethylpyrogallol; 4-hydroxy-3-methoxytoluene, 4-hydroxy-3-methoxystyrene Eugenol; cis-Isoeugenol; trans-Isoeugenol; Vanillin; acetovanillone; pyrogallol 1,3-dimethylether; 4-hydroxy-3,5-dimethoxytoluene, 4-hydroxystyrene; 4-hydroxy-3-methoxystyrene; 4-hydroxy-3-methoxy-1-vinylbenzene; 4-hydroxy-3,5-dimethoxy-1-ethylbenzene; 4-hydroxy-3-methoxy-1-vinylbenzene; benzene; sinasaaldehyde; coniferaldehyde; syringaldehyde; allylsyringol; methylnaphthalene ; p-ethylphenol; 2,4,6-trimethylphenol; α-naphthol; p-hydroxybenzaldehyde; p-hydroxyacetophenone; acetosyringone; butyrolactone; crotonic acid, maltol; 2-hydroxy-3-methyl-Δ2-cyclopentenone; 2,6-dimethoxyphenol; tiglaldehyde; methyl isopropyl ketone; methyl ethyl ketone; methyl furyl ketone; acetaldehyde; furan; 2,3-butandione; methylfuran; 1-hydroxy-2-propanone; glyoxal; acetic acid; furfural; acetone; propionaldehyde; methanol; 3-hydroxy-2-butanone; ethanol; diacetyl; furfuryl alcohol; formaldehyde; 1-butanol; isobutyl alcohol; anthracene; and phenanthrene..[3-14]

Our objectives were to develop methods for determining the chemical composition of the pyrolytic oils immediately after collection and then to observe any changes in the chemical composition of the oils as a function of increasing viscosity. Also, after the mechanism of the increase in viscosity of the pyrolytic oils had been determined, attempts were to be made to stabilize the pyrolytic oils against whatever changes they undergo.

Therefore, our objectives were:

1. To develop, jointly, combined gas chromatographic-mass spectrometric and liquid chromatographic methods for the determination of the chemical composition of the pyrolytic oils.
2. To determine the mechanism of the increase in viscosity of the pyrolytic oils.
3. To develop a stabilized pyrolytic oil composition.
4. To evaluate pyrolytic oils as a feed stock for the recovery and production of chemicals.
5. To routinely analyze pyrolytic oil samples submitted by the pyrolytic oil research group at the Engineering Experiment Station at the Georgia Institute of Technology.

SECTION 2

CONCLUSIONS

1. Distillation, column chromatography, and filtration were the sample preparation techniques used. Filtration was found to be the approach which resulted in the highest recovery of oil. Filtration resulted in a 96% recovery; vacuum distillation, 64%; column chromatography, 56%.
2. Packed column gas chromatography gave sufficient resolution for combined gas chromatographic-mass spectrometric analysis but considerable peak overlap occurred. Capillary gas chromatography gave superior resolution. Peak enhancement studies were much more successful when capillary gas chromatography methods were used.
3. Liquid chromatography of the pyrolytic oils using reverse phase gradient elution techniques produced low resolution chromatograms which were, however, amenable to peak enhancement studies.
4. Increasing viscosities of the pyrolytic oils were accompanied by the disappearance of low molecular weight aldehydes, ketones, carboxylic acids and polymerizable olefins. The increases in viscosity are due to polymerization of olefins such as 4-hydroxy-3-methoxystyrene, Anethole, Estragole, Eugenol, and Isoeugenol and possibly evaporation.
5. The pyrolytic oils were readily hydrogenated to develop an oil which would be stable to cationic chain-reaction polymerization in acid solution.
6. The pyrolytic oils are an excellent feed stock for the recovery and production of chemicals. The pyrolytic oils were easily separated into various chemical classes. The phenolic fraction may be polymerized to produce a phenolic resin.
7. Routine analysis of pyrolytic oil samples is accomplished by filtration of the oils in acetone solution and capillary gas chromatographic or gas chromatographic-mass spectrometric analysis.

SECTION 3

RECOMMENDATIONS

Routine analysis of pyrolytic oil samples would be significantly improved by substituting a capillary gas chromatograph for the packed column gas chromatograph in the combined gas chromatograph-mass spectrometer system.

The oil may be stabilized by hydrogenation or the increase in viscosity may be successfuly counteracted by adding a low viscosity solvent such as methanol or acetone to the pyrolytic oil. Increased water content also leads to lower viscosity pyrolytic oil samples. Refrigeration of the samples should aid in stabilizing the pyrolytic oils against evaporation.

The pyrolytic oils contain a number of valuable chemicals. Further investigations of the isolation of these valuable chemicals from the pyrolytic oils are recommended.

SECTION 4

DISCUSSION

Sample Preparation

Distillation:

Pyrolytic Oil (Project B-469 Condenser Oil) was vacuum distilled at 56° C/14.5mmm. - 188°C/19.0mm. At the higher temperature, significant decomposition occurred. One hundred and ninety-two grams of the pyrolytic oil were distilled to yield 87.2g (45.4% recovery) of a viscous yellow oil.

Project B-469 Condenser Oil was also vacuum distilled at 22°C/6.6mm-128°C/15.0 mm to produce a viscous yellow oil in 37% recovery.

Similarly, Project B-469 Draft Fan Oil was distilled at 24°/11.5mm-122°C/6.7mm to produce a viscous yellow oil in 17% recovery.

Column Chromatography

Project B-469 Condenser Oil (20.0g) was eluted from a 60mm by 25mm neutral alumina column (alumnia, Neutral Brockman Activity 1, 80-200 Mesh. Fisher Scientific) with tetrahydrofuran. The THF was evaporated at room temperature to produce 11.2g (56% recovery) of a brown viscous oil.

Filtration

Acetone was added to the pyrolytic oil sample (30g) until it was fluid enough for filtration. The solution was filtered under suction. A black semi-solid material (1.3g) was collected. The acetone solution was subsequently used for gas chromatographic analysis.

Combined Gas Chromatographic/Mass Spectrometric Analysis of the Pyrolytic Oils

GC/MS of Condenser Oil Distillate

Qualitative analysis of the condenser oil distillate by combined gas chromatography mass spectrometry was performed on a DuPont Model 21-490 GC-Mass Spectrometer. The GC conditions were: Column-6ft.x1/8 in. Se-30 stainless steel, Flow Rate-10 ml/min. He, Initial Temperature -25°C, Programming Rate - 4°C per min. Final temperature -200°C, Detector-Flame Ionization. The GC-MS scan is shown in Figure 1. The mass spectral results are listed in Table 1.

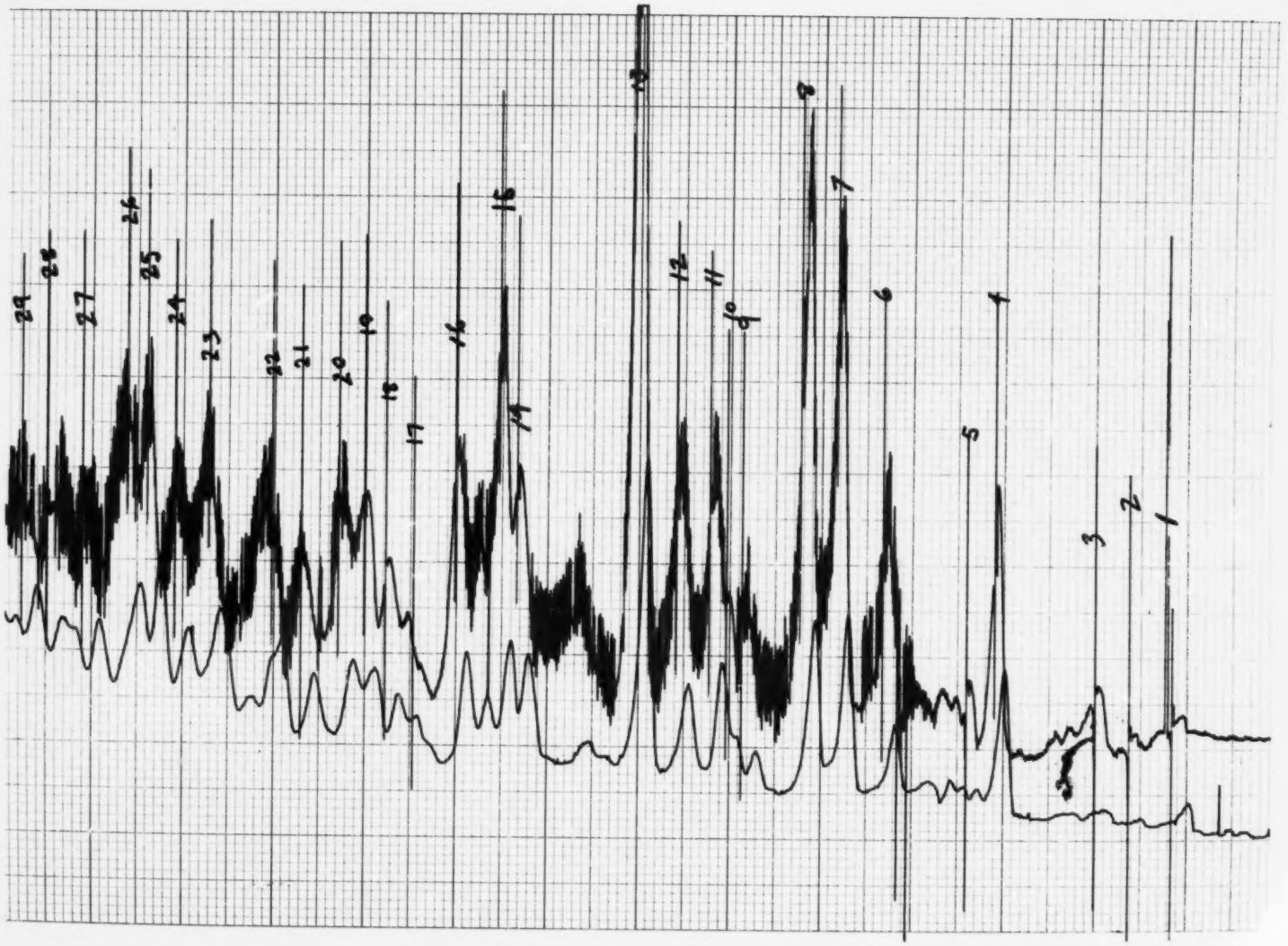

Figure 1. GC/MS of Pine Condenser Oil Distillate.

TABLE 1. GC/MS ANALYSIS OF CONDENSER OIL DISTILLATE

Scan No.	Components	m/e (Relative Intensity %)
1	Ethanol, Furfural, Acetaldenyde	29(66), 38(6), 39(14), 40(50), 41(100), 42(4), 43(7), 44(36), 45(24), 46(4), 69(4), 95(47), 96(50), 97(3)
2	Ethanol	29(49), 40(17), 41(100), 45(43) 46(26), 83(14), 95(3), 96(3)
3	Acetone, Heptanol	29(56), 41(63), 43(100), 45(17), 58(50), 87(5), 95(4), 100(6), 115(6), 116(8)
4	Phenol	29(18), 40(32), 41(23), 44(14), 65(20), 66(41), 93(1), 94(100), 95(5)
5	1-Octanol	29(75), 41(71), 44(100), 45(13), 58(69), 95(5), 97(5), 100(4)
6	o-Cresol, 5-Methylfurfural	29(55), 40(64), 41(98); 44(25), 56(29), 67(39), 77(34), 79(34), 107(59), 108(100), 110(20)
7	m-and p-Cresols	29(19), 40(31), 41(34), 44(14), 52(19), 56(16), 58(18), 69(13), 77(27), 29(29), 107(90), 108(100), 110(8)
8	Guaiacol	29(23), 40(27), 41(42), 54(25), 82(67), 109(100), 124(81), 125(4)
9	Veratrole	29(49), 40(31), 41(100), 44(45), 56(22), 95(28), 123(9), 138(8)
10	2,6 Dimethylphenol, Naphthalene	29(57), 40(38), 41(97), 44(33), 56(21), 91(19), 107(90), 121(48), 122(100); 128(24)
11	Naphthalene	29(19), 40(10), 41(31), 44(11), 52(13), 65(7), 77(5), 102(6), 127(11), 128(100), 129(9)
12	Estragole, Naphthalene, 2,4-Dimethylphenol	29(42), 40(53), 41(83), 42(43), 69(29), 77(34), 91(21), 107(100), 122(49), 128(52), 147(33), 148(33), 149(8)
13	2-Methoxy-4-methylphenol	29(10), 40(19), 41(12), 42(15), 52(13), 54(7), 56(18), 65(10), 66(10), 67(19), 77(16), 95(37), 107(4), 121(1) 123(87), 124(6), 137(7), 138(100), 139(9)
14	Methylnaphthalene, 2-Methoxy-4-ethylphenol	29(32), 40(32), 41(77), 44(31), 77(22) 91(24), 108(22), 109(25), 115(35), 138(38), 141(73), 142(100), 152(46)

-continued-

TABLE 1 (continued)

Scan No.	Components	m/e (Relative Intensity %)
15	2-Methoxy-4-ethylphenol	29(18), 40(19), 41(32), 42(12), 44(15), 77(13), 91(17), 122(12), 137(100), 138(8), 152(47)
16	Unknown	29(54), 40(46), 41(94), 42(100), 44(55), 56(55), 67(32), 69(72), 77(19), 79(45), 81(45), 91(41), 93(61), 132(37)
17	Unknown	29(46), 40(36), 41(100), 42(58), 44(56), 58(27), 77(26), 91(22), 93(71), 152(23)
18	2-Methoxy-4-propyl-phenol, Eugenol	29(47), 40(39), 41(100), 42(58), 44(56), 56(38), 77(40), 91(32), 137(100), 164(57), 166(23)
19	cis-Isoeugenol, Dimethylnaphthalene	29(48), 40(34), 41(100), 42(37), 44(49), 91(36), 119(29), 142(43), 148(24), 156(30), 158(41), 164(63)
20	Dimethylnaphthalene	29(42), 40(28), 41(100), 42(38), 44(46), 56(32), 58(31), 142(45), 155(19), 156(83)
21	trans-Isoeugenol, Dimethylnaphthalene	29(49), 32(34), 40(100), 41(54), 42(67), 44(33), 56(54), 58(22), 91(21), 153(21), 154(40), 156(36), 158(24), 164(31)
22	trans-Isoeugenol, Vanillin	29(49), 40(46), 41(100), 42(55), 44(67), 56(57), 58(38), 69(19), 77(40), 91(39), 152(81), 164(86)
23	Unknown	29(47), 40(35), 41(100), 42(54), 44(64), 56(38), 58(39), 69(26), 77(29), 91(27), 152(36), 153(35), 154(35), 178(42)
24	Hydroquinone	29(50), 40(38), 41(99), 42(99), 44(87), 56(98), 58(67), 69(59), 81(51), 95(40), 110(100)
25	Allynaphthalene	29(38), 40(23), 41(73), 42(58), 44(69), 56(62), 58(71), 69(39), 139(32), 168(100), 169(15), 170(12)
26	Allylnaphthalene	29(45), 40(29), 41(100), 42(74), 44(75), 56(55), 58(54), 69(41), 71(33), 167(36), 168(37), 169(14)

GC/MS of Condenser Oil Column Eluate

The gas chromatographic-mass spectrometric analysis of the column

eluates was performed on a DuPont Model 21-490 GC-Mass spectrometer. The GC conditions were the same as those for the analysis of the distillate. The GC-MS scan is shown in Figure 2. The mass spectral results are listed in Table 2.

TABLE 2. GC/MS of Condenser Oil Column Eluate

Scan No.	Components	m/e (Relative Intensity %)
1	Ethanol, Acetaldehyde, Isobutyl Alcohol	29(11), 32(54), 39(2), 40(8), 41(4), 42(18), 43(41), 44(11), 45(12), 46(3), 47(2) 56(2), 60(3), 61(3), 71(3), 73(81), 74(100), 75(12), 116(2)
2	Ethanol, Acetaldehyde, Isobutyl Alcohol	29(22), 31(10), 39(5), 41(27), 42(17), 43(61), 44(100), 45(24), 46(71), 73(31), 74(31)
3	Acetone, Acetic Acid, 1-Butanol, a Butyric Acid	29(25), 31(37), 32(72), 38(3), 39(6), 40(32), 41(17), 42(56), 43(100), 44(16) 45(20), 46(13), 48(7), 58(21), 59(9), 60(7), 72(12), 73(20), 74(8), 88(4)
4	Phenol	39(11), 40(31), 41(19), 56(10), 66(26), 67(35), 94(100), 96(9)
5	o-Cresol	29(26), 40(27),41(51), 77(34), 79(36), 91(24), 107(72), 108(100), 109(9)
6	m-and-p-Cresols	29(10), 40(22), 41(14), 42(9), 51(10), 52(16), 54(14), 77(30), 78(10), 79(28) 80(12), 91(11), 92(17), 107(85), 108(100), 109(10)
7	Guaiacol	29(11), 40(20), 41(15), 54(26), 81(74), 108(100), 109(11), 124(61), 125(8)
8	2,4-Dimethylphenol and/or 3,5-Dimethylphenol	29(25), 40(33), 41(48), 77(34), 79(26), 91(27), 107(92), 121(50), 122(100)
9	Veratrole, Naphthalene, Dimethylphenol	29(19), 40(26), 41(31), 52(22), 77(33), 78(12), 79(13), 81(8), 91(13), 93(7), 94(8), 95(8), 107(100), 108(12), 121(14), 122(56), 123(17), 126(9), 127(13), 128(76), 129(12), 138(12)
10	2-Methoxy-4-methylphenol	29(8), 40(24), 42(16), 56(20), 67(26), 77(20), 95(36), 123(84), 138(100), 139(10)
11	2-Methoxy-4-ethylphenol	29(41), 40(46), 41(81), 109(44), 137(81) 152(100), 153(18)
12	2-Methoxy-4-ethylphenol	32(93), 40(12), 41(9), 65(9), 77(11), 91(13), 94(10), 122(12), 137(100), 138(10), 152(47)

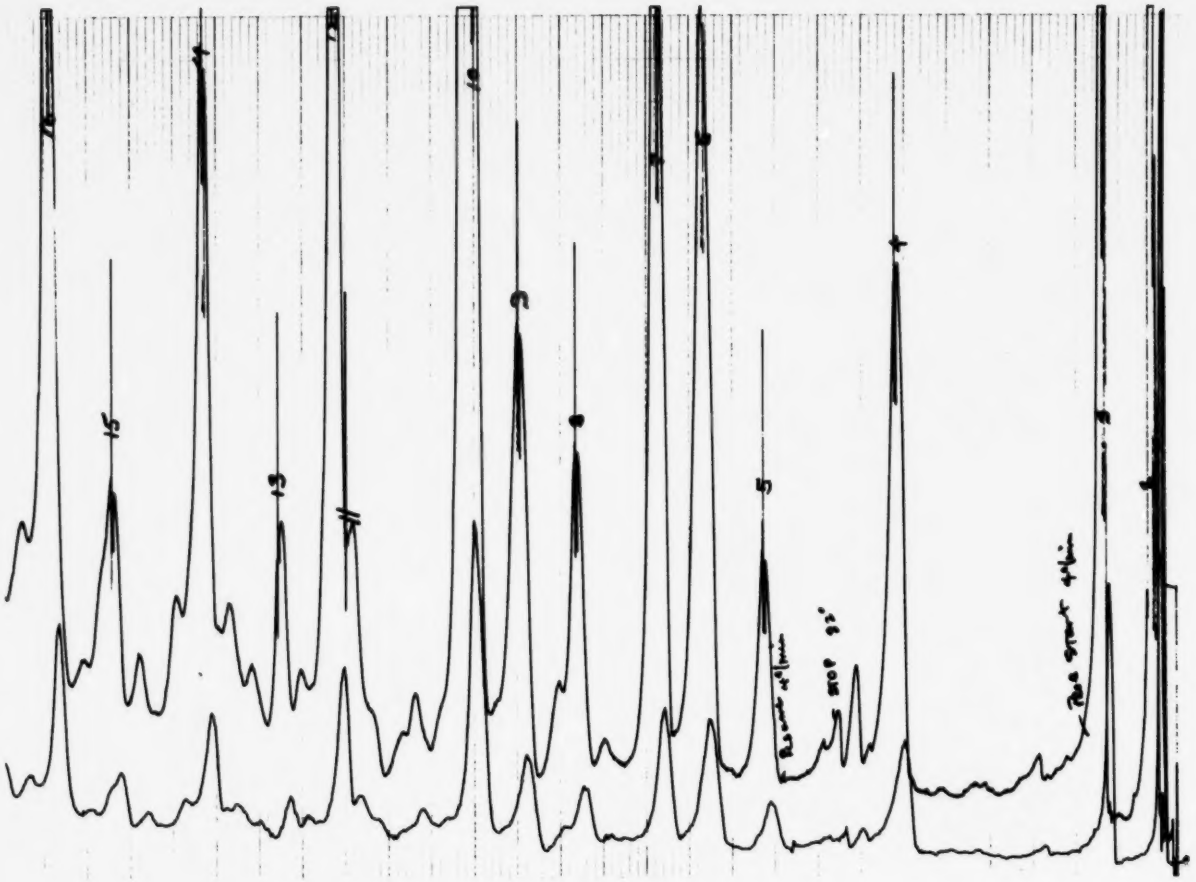

Figure 2. GC/MS of Pine Condeser Oil Column Eluate.

TABLE 2 (continued)

Scan No.	Components	m/e (Relative Intensity %)
13	Anethole, Unknown	29(43), 40(42), 41(100), 42(94), 43(19), 44(40), 45(26), 52(18), 54(27), 56(38), 58(21), 65(20), 67(32), 69(55), 77(32), 79(40), 80(18), 81(38), 82(18), 83(21), 91(41), 92(19), 93(48), 94(19), 95(26), 105(29), 106(20), 107(30), 108(19), 109(22) 118(21), 119(22), 121(50), 122(19), 134(36) 135(19), 136(19), 138(22), 148(19), 149(19) 160(19)
14	2-Methoxy-4-propylphenol, Eugenol	29(15), 40(24), 41(21), 77(30), 91(19), 133(24), 134(22), 137(100), 149(21), 164(47), 166(29)
15	cis-Isoeugenol	29(49), 40(48), 41(87), 56(55), 77(57), 91(49), 149(72), 164(100), 165(19)
16	trans-Isoeugenol	29(9), 40(14), 41(11), 56(28), 65(13), 77(32), 91(27), 103(27), 104(13), 121(21) 131(21), 133(14), 149(46), 164(100), 165(13).

GC/MS of Standards

In order to establish the validity of some of our assignments the gas chromatographic-mass spectrometic analysis of mixtures of standards was obtained under the same conditions described earlier. The results are described in Table 3.

TABLE 3. Mass Spectra of Authenic Known Samples Run on DuPont Model 21-490

Sample	m/e (Relative Intensity %)
1-Butanol	29(32), 31(60), 33(4), 39(17), 40(22), 41(82), 42(16), 43(40), 44(6), 45(8), 54(16), 55(100), 56(11), 73(6), 74(30),
Isobutyric Acid	29(10), 31(4), 39(16), 40(16), 41(50), 42(14), 43(100), 44(5), 45(15), 55(8), 56(3), 57(3), 74(30), 75(2), 88(10)
Butyric Acid	33(14), 36(74), 43(18), 45(18), 46(18), 47(18), 49(18), 59(9), 63(100), 76(23), 88(16)
5-Methylfurfural	31(38), 36(11), 43(20), 45(85), 46(55), 47(75) 57(13), 59(85), 60(100), 61(50), 72(50), 73(58), 86(25), 87(50), 110(12)

TABLE 3 (continued)

Sample	m/e (Relative Intensity %)
1-Heptanol	29(38), 31(25), 41(96), 42(56), 43(68), 54(68), 55(100), 56(30), 69(56), 70(96), 73(66), 84(25), 99(7), 100(8)
2,3-Dimethylphenol	31(11), 36(30), 43(17), 45(12), 54(14), 56(10), 79(17), 80(11), 81(17), 93(17), 107(75), 122(100)
2,4-Dimethylphenol	31(2), 94(10), 107(60), 121(30), 122(100)
2,6-Dimethylphenol	36(6), 43(8), 55(6), 80(25), 82(22), 94(20), 107(40), 122(100)
Naphthalene	36(13), 43(25), 54(6), 67(5), 104(7), 128(100)
2-Methoxy-4-methylphenol	31(16), 35(44), 45(41), 54(14), 55(30), 56(14), 57(14), 59(30), 68(20), 69(20), 70(30), 80(22), 81(18), 95(58), 123(100), 138(100)
Veratrole	29(4), 41(18), 52(12), 63(10), 64(12), 65(12), 93(38), 123(100), 138(97), 139(10)
m-Dimethoxybenzene	29(8), 38(16), 39(30), 40(44), 41(46), 42(22), 43(22), 50(18), 51(18), 52(36), 53(10), 62(26) 63(26), 64(30), 67(12), 77(30), 78(30), 79(12), 80(16), 81(29), 91(16), 92(12), 94(72), 107(20), 108(32), 123(66), 138(100), 139(10)
Anethole	31(5), 36(5), 43(5), 55(6), 60(5), 66(6), 80(10), 107(13), 133(15), 148(100)
2,5-Dimethoxytoluene	29(26), 39(12), 43(22), 65(10), 66(10), 77(14), 92(10), 94(10), 108(18), 137(100), 152(84)
2-Hydroxy-4-methoxybenzaldehyde	39(16), 63(10), 81(10), 95(14), 151(100), 152(100), 153(11)
3,4-Dimethoxyphenol	33(8), 36(8), 42(7), 54(5), 55(7), 56(7), 57(7), 59(7), 68(16), 71(16), 82(5), 84(7), 96(10), 98(10), 114(24), 139(60), 154(100)
2,3-Dimethylnaphthalene	36(7), 66(5), 79(6), 80(22), 116(7), 127(5), 128(7), 142(50), 143(6), 156(100)
Eugenol	31(5), 43(10), 59(17), 80(17), 94(16), 106(10), 107(10), 123(58), 132(10), 134(10), 137(17), 149(23), 164(100)
Isoeugenol	39(13), 51(10), 77(24), 91(20), 102(20), 103(13) 120(15), 130(13), 132(12), 137(30), 164(100)
2-Methoxy-4-propylphenol	36(8), 43(6), 55(6), 80(6), 96(8), 124(10), 137(100), 166(30)
2-Hydroxy-methoxyacetophenone	29(45), 43(16), 51(11), 95(18), 107(11), 151(100), 166(72)

Gas Chromatographic-Packed Column Peak Enhancement Studies

The condenser oil distillate was analyzed on an Aerograph 1440 Gas Chromatograph with a flame ionization detector. The chromatogram is shown in Figure 3. The conditions were: A 10-ft. by 1/8 in. stainless steel column packed with 2% OV-17 and 1% OV-210 on 100/120 mesh Supelcoport F-01409, oven temperature program-50°-225°C at 10°C per min.,

He flow rate-30ml/min. Peak identifications were made by noting the enhancement of peak size when known substances were chromatographed with the distillate. Peak assignments are described in Table 4.

TABLE 4. Condenser Oil Distillate Packed Column Peak Enhancement Results

Peak No.	Assignments
1	Ethanol, Acetone, Acetaldehyde
3	1-Butanol, Acetic Acid
4	1-Pentanol
6	Isobutyric Acid
7	Butyric Acid
9	Furfural
12	1-Heptanol
13	2-Octanol
15	Phenol
16	5-Methylfurfural, 1-Octanol
18	o-Cresol
19	Unknown
20	m-and p-Cresol
21	Hydroquinone
22	Guaiacol
23	2,4-Dimethylphenol and/or 3,5-Dimethylphenol
24	Estragole, Veratrole, Naphthalene, m-and p-Dimethoxybenzene
25	2-Methoxy-4-methylphenol
26	2,5-Dimethoxytoluene
28	m-and p-Methoxyphenol
29	Anethole, Methylnaphthalene
32	2-Methoxy-4-propylphenol, Eugenol
35	cis-Isoeugenol, Dimethylnaphthalene
37	trans-Isoeugenol
39	Vanillin

Figure 4 is the packed column gas chromatogram of the draft fan oil distillate. The conditions were the same described previously for the condenser oil distillate. The chromatograms of the two distillates are quite similar. The major peaks, essentially, appear at the same retention times.

Composition of Distillate as a Function of Time

The condenser oil distillate was distilled at 22°C/6.6mm-128°C/15.0mm on November 8, 1976. Figure 3 is the gas chromatogram of that distillate on March 3, 1977. Peaks, 3,4,8,12,13, and 16 were alcohols. Peaks 3,6, and 7 were carboxylic acids. Peaks 9 and 16 were aldehydes,

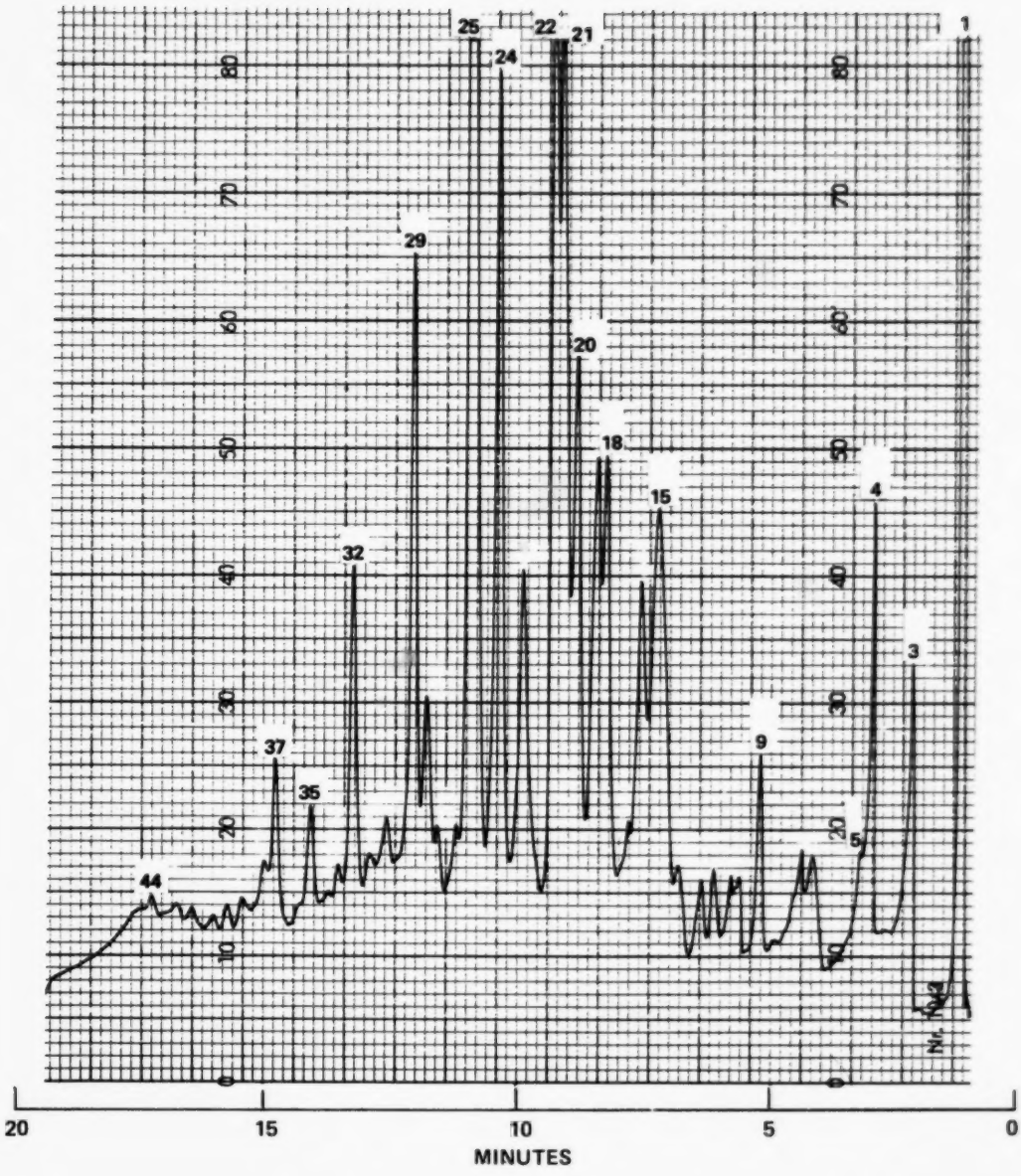

Figure 3. Gas Chromatogram of Pine Condenser Oil Distillate (March 3, 1977).

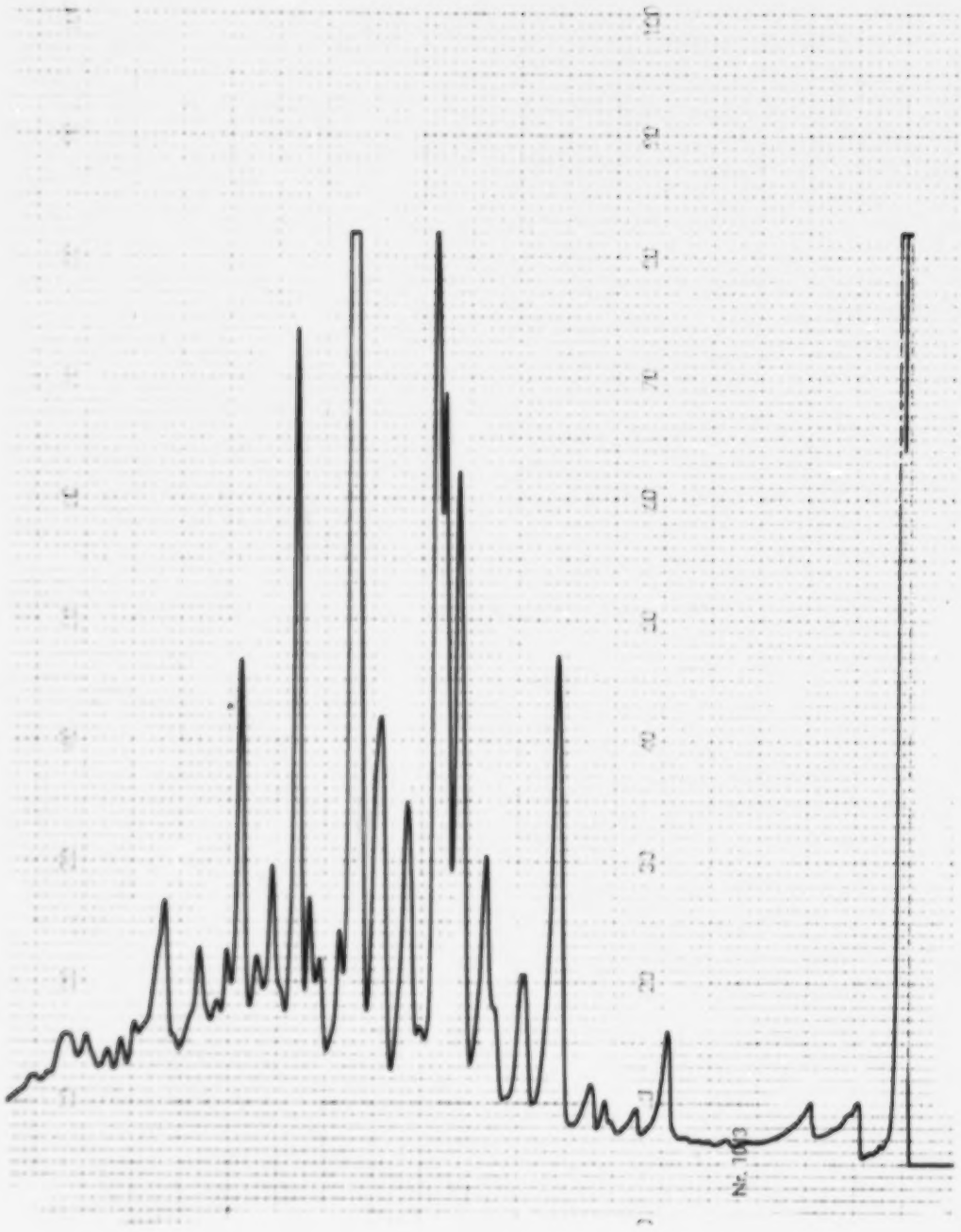

Figure 4. Gas Chromatogram of Pine Draft Fan Oil Distillate (June 30, 1977).

In Figure 5, the gas chromatogram of the condenser oil distillate on on August 17, 1977, peaks 3,4,6,7,8,9,12,13, and 16 were decreased significantly in area.

The decreases in area of the alcohol and carboxylic acid peaks are due to the formation of esters under acidic conditions over a period of time. The decreases in area of the alcohol and aldehyde peaks are due to the formation of acetals under acidic conditions over a period of time. These conclusions are in agreement with the observation of J. Knight[15] that there was an increase in water content for a pyrolytic oil sample stored over a period of eight months.

Also, we noticed that peak 24 (Veratrole, naphthalene, m-and p-dimethoxybenzene, and Estragole) decreased significantly in area from March 3, 1977 to August 17, 1977. The decrease in area of that peak was possibly due to the cationic chain-reaction polymerization of Estragole (4-allylanisole) under the acidic conditions (ph=3). This would account for the increase in viscosity of the pyrolytic oils on heating noted by J. Knight.[15]

Other olefins present in the pyrolytic oils which could undergo cationic chain-reaction polymerization, especially under the influence of the high temperatures used for distillation and the low ph, were Isoeugenol (2-methoxy-4-propenylphenol), Eugenol (4-allyl-2-methoxyphenol) and Anethole (p-propenylanisole). To test our hypothesis concerning the facility of cationic chain-reaction polymerization of these olefins, Anethole, Estragole, Eugenol, and Isoeugenol were separately added to 3MHCl solutions. Isoeugenol formed a solid precipitate overnight. Eugenol formed a brown viscous gel. Anethole and Estragole formed brown oils.

In order to do a better job of following the changes in composition, a higher resolution gas chromatographic technique was needed. As a result, a capillary gas chromatographic assay was developed for the pyrolytic oils.

Capillary Gas Chromatography of the Pyrolytic Oils

The condenser oil distillate was analyzed on a Varian 3740 capillary gas chromatograph with a flame ionization detector. The chromatogram is shown in Figure 6. The conditions were: A 30 meter Supelco 2-3700 glass capillary grade AA SP2100 column (internal diameter ca. 0.25mm), oven temperature program -40° C-220°C at 5°C per min. He flow rate-1.0ml/min. The chromatogram was determined in the direct injection mode. Peak identifications were made by noting the ehancement of peak size when known substances were chromatographed with the distillate. Peak assignments and quantitative data are presented in Table 5.

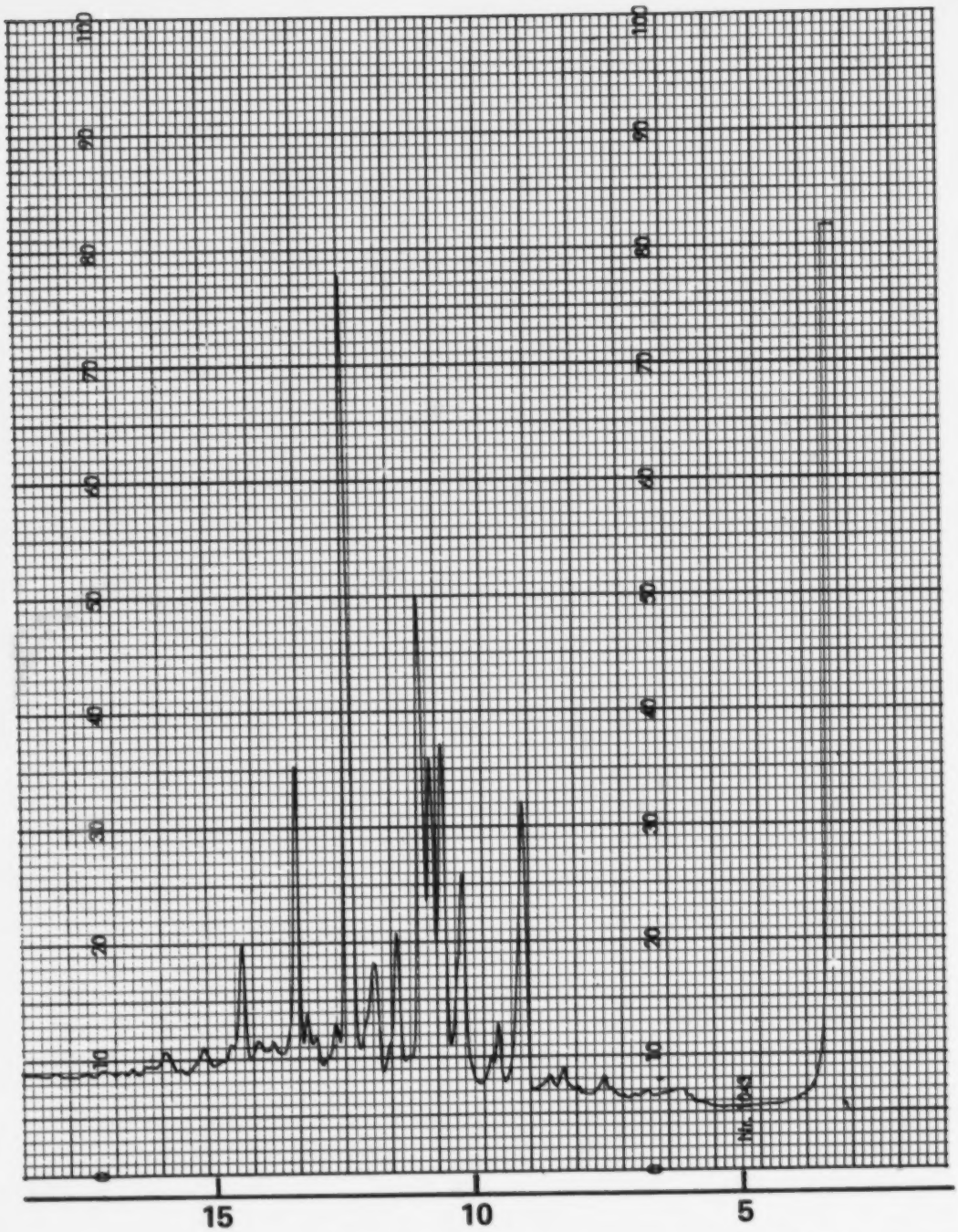

Figure 5. Gas Chromatogram of Pine Condenser Oil Distillate (August 17, 1977).

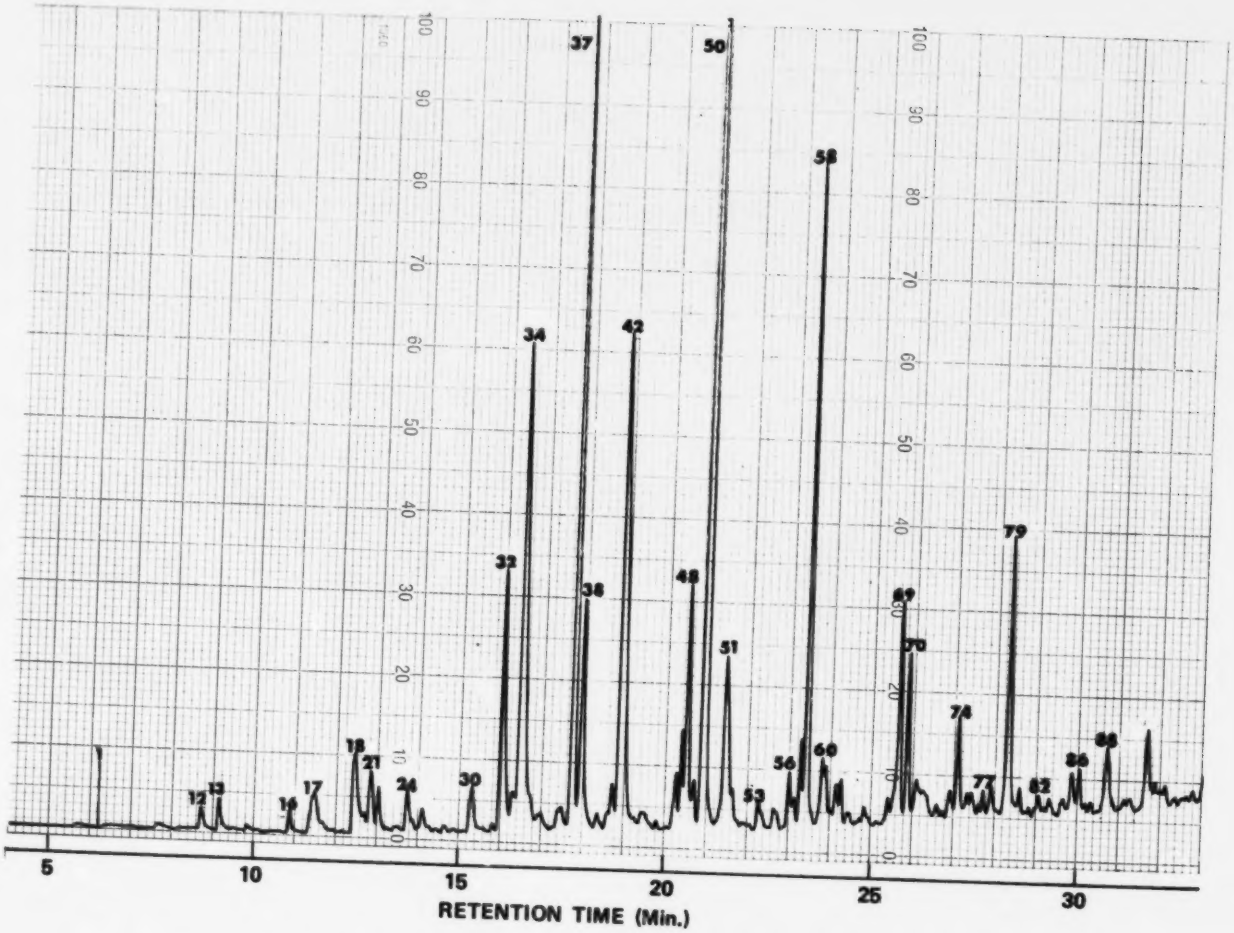

Figure 6. Capillary Gas Chromatogram of Pine Condenser Oil Distillate (Distillation - July 23, 1976; GC-June 13, 1978).

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TABLE 5. Condenser Oil Distillate Peak Enhancement Results from Capillary Column

Peak No.	Retention Time (min)	GC %	Assignment
13	9.2	0.27	Furfural
17	11.5	0.71	Furfuryl Alcohol
21	12.8	0.36	5-Methylfurfural
30	15.3	0.76	2-Octanol
34	16.4	5.67	Phenol
37	17.7	4.71	Guaiacol
38	17.9	2.50	o-Cresol
42	18.8	5.97	m-and p-Cresol
48	20.5	2.72	Naphthalene
50	20.9	10.40	2-Methoxy-4-methyphenol
51	21.4	3.00	Dimethylphenol
58	23.4	4.83	2-Methoxy-4-ethylphenol
69	25.6	2.20	Eugenol
70	25.9	1.69	2-Methoxy-4-propylphenol
79	28.3	3.08	Isoeugenol

The condenser oil column eluate was also analyzed on the Varian 3740 Capillary Gas Chromatograph under the same conditions. The chromatogram is shown in Figure 7. Peak assignments and quantitative data are presented in Table 6.

TABLE 6. Condenser Oil Column Eluate Capillary Gas Chromatogram Results

Peak No.	Retention Time (Min)	GC %	Assignment
2	4.5	11.35	Esters
13	9.1	0.46	Furfural
17	11.4	5.16	Furfuryl Alcohol
21	13.0	0.34	5-Methylfurfural
30	15.2	0.43	2-Octanol
34	16.4	6.79	Phenol
37	17.17	4.36	Guaiacol
38	18.0	1.88	o-Cresol
42	18.9	5.65	m-and p-Cresol
48	20.5	1.80	Naphthalene
50	20.9	9.06	2-Methoxy-4-methylphenol
51	21.4	2.83	Dimethylphenol
58	23.4	3.77	2-Methoxy-4-ethylphenol
69	25.7	1.94	Eugenol
70	25.9	1.92	2-Methoxy-4-propylphenol
79	28.4	1.76	Isoeugenol

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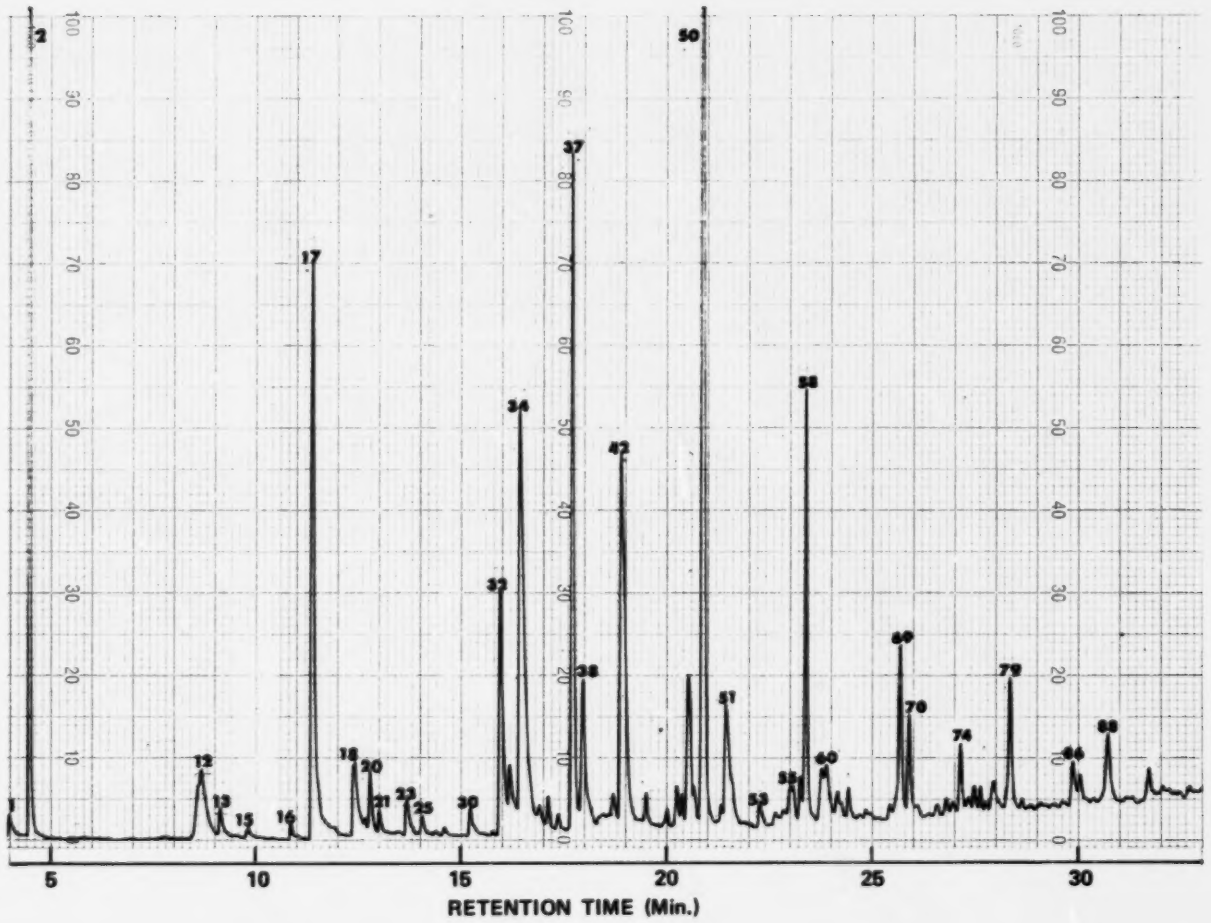

Figure 7. Capillary Gas Chromatogram of Pine Condenser Oil Eluate (Column Chromatography-September 30, 1977; GC-May 10, 1978).

A fresh sample of pyrolytic oil obtained from the Blue IV pilot plant at the Georgia Institute of Technology Engineering Experiment Station was dissolved in acetone, filtered, and the filtrate was analyzed on the Varian 3740 Capillary Gas Chromatograph. The run had been made on June 14, 1978. On June 16, 1978, the filtrate had the chromatogram shown in Figure 8. Peak assignments and quantitative data are presented in Table 7.

TABLE 7. Condenser Oil Filtrate Capillary Gas Chromatogram Results

Peak No.	Retenction Time (Min)	GC %	Assignment
3	5.6	0.76	Isobutyl Alcohol
4	5.8	1.95	1-Butanol
13	9.2	1.81	Furfural
17	11.5	1.45	Furfuryl Alcohol
21	13.0	0.62	5-Methylfurfural
30	15.3	2.18	2-Octanol
34	16.4	4.63	Phenol
37	17.7	5.15	Guaiacol
38	18.0	1.02	o-Cresol
42	18.9	7.90	m-and p-Cresol
48	20.5	1.24	Naphthalene
50	20.9	12.98	2-Methoxy-4-methylphenol
51	21.4	1.29	Dimethylphenol
58	23.4	2.19	2-Methoxy-4-ethylphenol
64	24.7	2.82	4-Hydroxy-3-methoxystyrene
66	25.1	2.08	Unknown
69	25.7	1.69	Eugenol
70	25.9	1.17	2-Methoxy-4-propylphenol
79	28.4	8.91	Isoeugenol

The pyrolytic oil (50g) in 200 ml. of ethyl acetate was reacted with 41 psi hydrogen in a Parr hydrogenation unit over ca. 1g Pd on charcoal for 16 hours. The pressure in the bottle when the reaction was stopped was 25 psi. The product in ethyl acetate was filtered and the ethyl acetate evaporated in vacuo. The brown oil obtained was analyzed on the Varian 3740 Capillary Gas Chromatograph. On July 13, 1978, the red-brown oil had the chromatogram shown in Figure 9. Peak assignments and quantitative data are presented in Table 8.

TABLE 8. Hydrogenated Condenser Oil Capillary Gas Chromatogram Results

Peak No	Retention Time (Min.)	GC %	Assignment
3	5.4	0.51	Isobutyl Alcohol

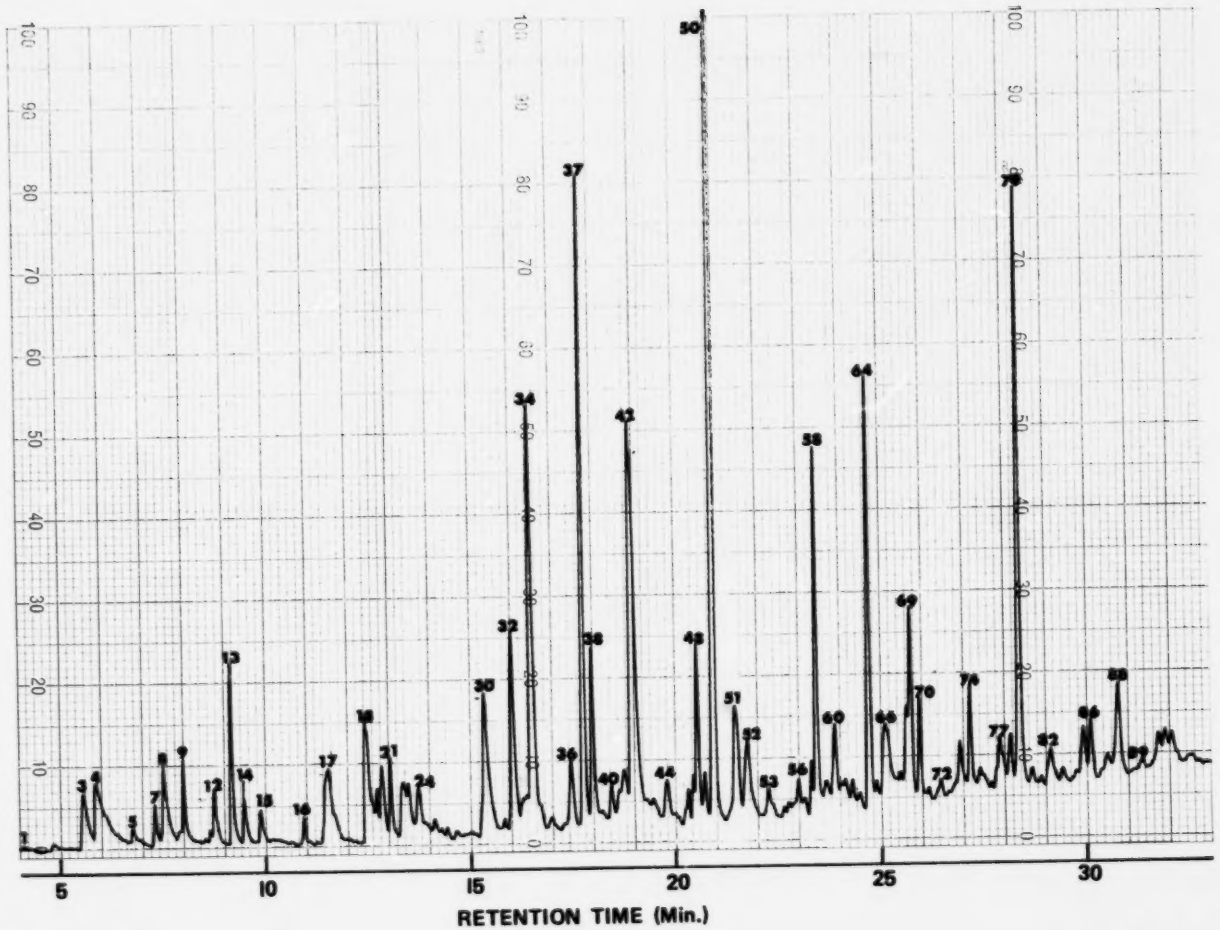

Figure 8. Capillary Gas Chromatogram of Pine Condenser Oil Filtrate (June 16, 1978).

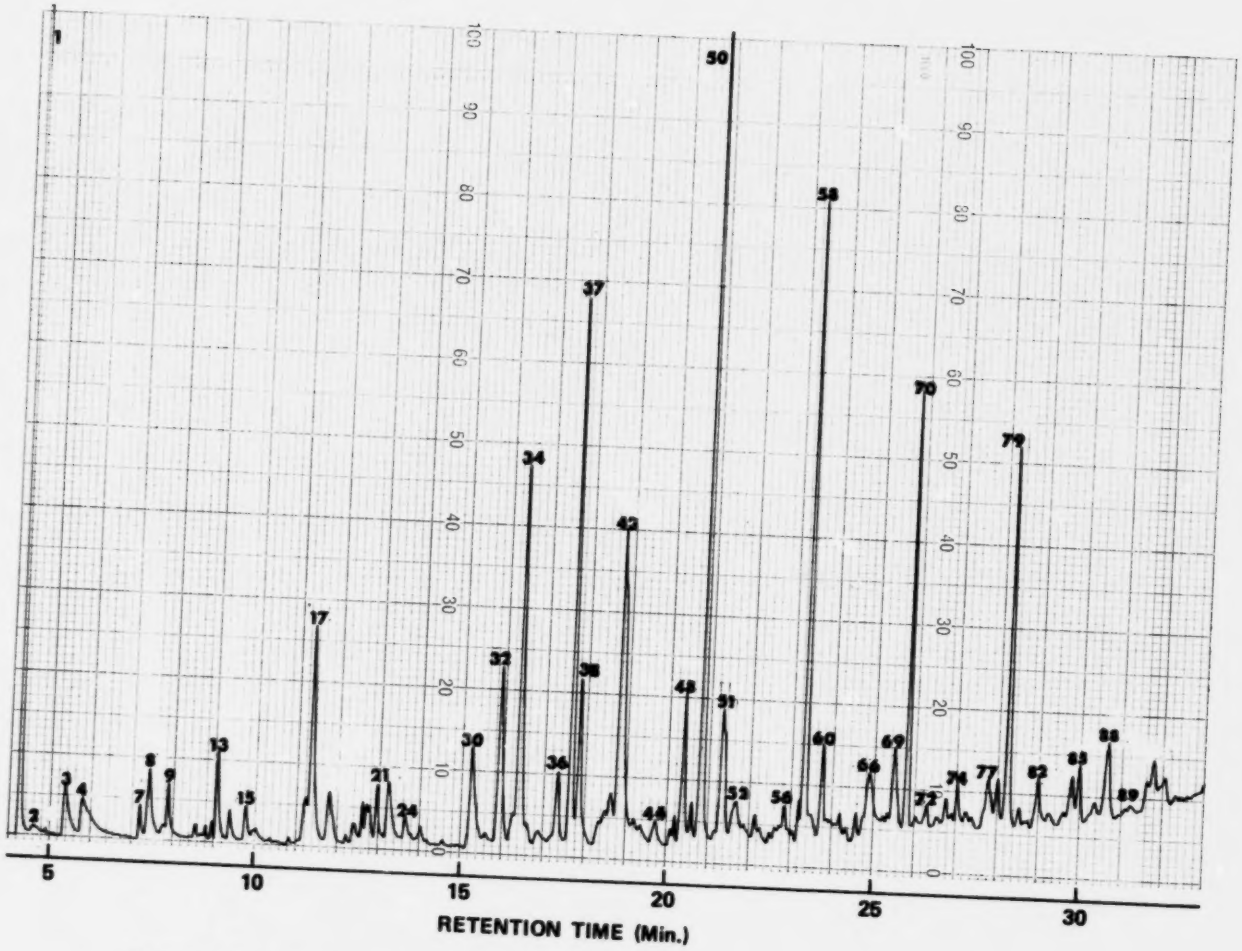

Figure 9. Capillary Gas Chromatogram of Hydrogenated Pine Condenser Oil Filtrate (Hydrogenation - July 12, 1978; GC-July 13, 1978).

TABLE 8 (continued)

Peak No.	Retention Time (Min.)	GC %	Assignment
4	5.8	0.81	1-Butanol
13	9.1	0.52	Furfural
17	11.3	1.95	Furfuryl Alcohol
22	13.2	0.86	5-Methylfurfural
30	15.2	1.18	2-Octanol
34	16.4	3.31	Phenol
37	17.6	3.02	Guaiacol
38	17.8	1.76	o-Cresol
42	18.8	5.55	m-and p-Cresol
48	20.4	1.35	Naphthalene
50	20.8	7.54	2-Methoxy-4-methylphenol
51	21.3	1.39	Dimethylphenol
58	23.3	3.88	2-Methoxy-4-ethylphenol
66	24.9	0.54	2-Hydroxy-4-methoxybenzaldehyde
69	25.5	1.64	Eugenol
70	25.8	2.97	2-Methoxy-4-propylphenol
79	28.2	3.37	Isoeugenol

Hydrogenation reduced the amount of Isoeugenol and Eugenol in the pyrolytic oil filtrate and should be effective in decreasing the amount of polymerization.

Figure 10 shows the capillary gas chromatogram of Eucalyptus oil. Peak assignments and quantitative data are presented in Table 9.

TABLE 9. Eucalyptus Condenser Oil Filtrate Capillary Gas Chromatogram Results

Peak No.	Retention Time (Min)	GC %	Assignment
4	5.5	0.92	Isobutyl Alcohol
5	5.6	10.06	1-Butanol
17	9.2	3.05	Furfural
24	11.6	1.81	Furfuryl Alcohol
40	16.2	2.66	Phenol
47	17.9	3.00	Guaiacol
48	18.1	0.58	0-Cresol
50	18.9	1.14	m-and p-Creosol
58	21.1	5.54	2-Methoxy-4-methylphenol
73	25.2	1.79	Eugenol
74	25.8	9.19	2-Methoxy-4-propylphenol
80	28.3	4.13	Isoeugenol

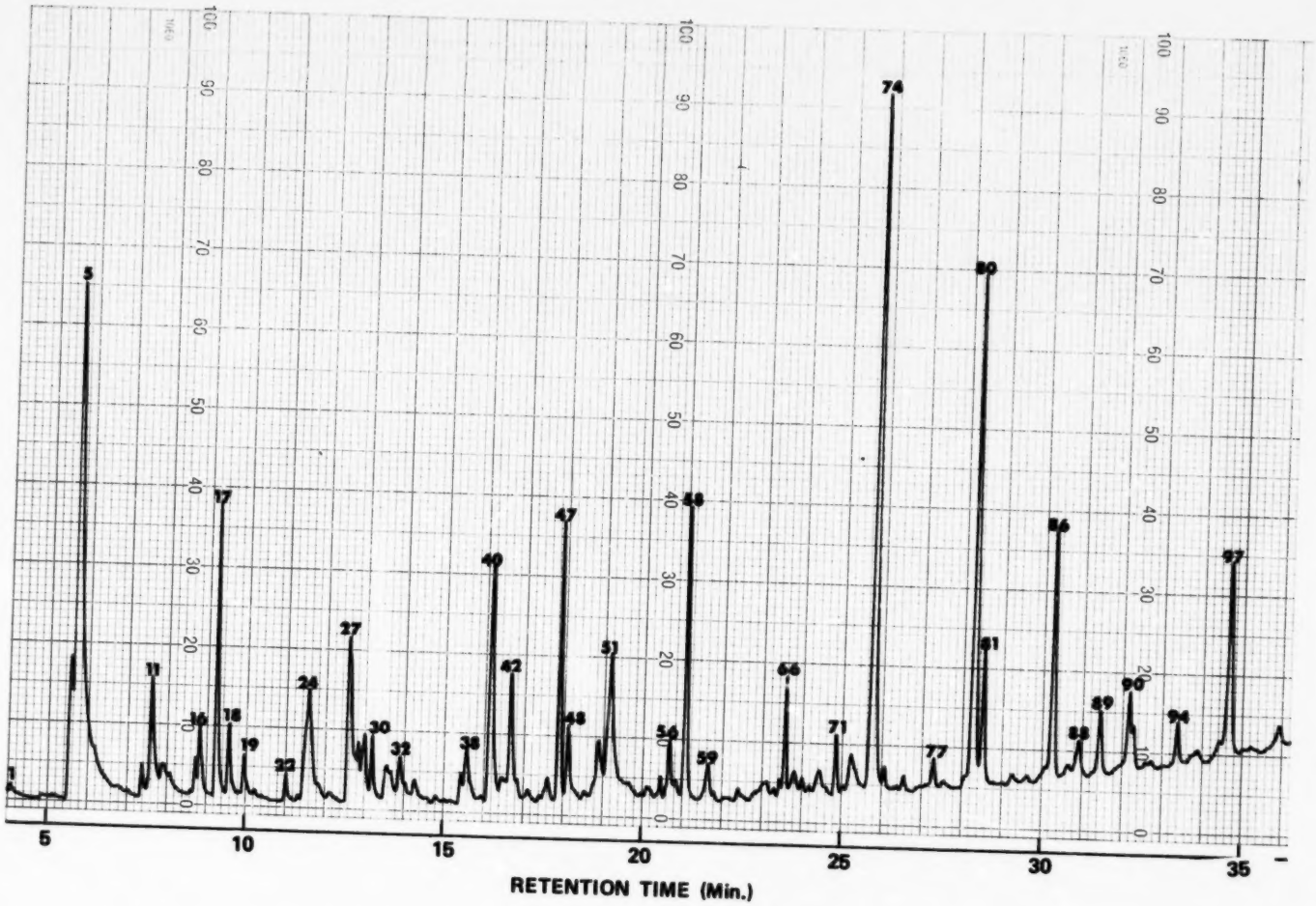

Figure 10. Capillary Gas Chromatogram of Eucalyptus Oil.

Liquid Chromatography of Condenser Oil Column Eluate

The condenser oil column eluates were analyzed on an Aerograph Model 8500 Liquid Chromatograph using an Aerograph Micropak CH-10 column. Reverse phase gradient elution chromatography from pure water to 50:50 acetonitrile-isopropanol at a flow rate of 2ml/min. gave the best results (see Figure 11). Although the liquid chromatogram was low in resolution, the peaks were identified by noting enhancement of peak size when known materials were added to the column eluates. Peak identifications are described in Table 10.

TABLE 10. Liquid Chromatographic Peak Enhancement Results for the Condenser Oil Eluate

Peak No.	Component
2	Hydroquinone
3	Furfural
4	Phenol
5	p-Methoxyphenol and 5-Methylfurfural
6	Guaiacol
7	m-Methoxyphenol
9	o-Cresol
10	p-Cresol
11	m-Cresol
12	Veratrole
14	m-Dimethoxybenzene and Eugenol
15	Isoeugenol
16	2-Methoxy-4-propylphenol
18	p-Dimethoxybenzene
19	Naphthalene

Routine GC/MS/DS Analysis of Pine Pyrolytic Oils

We have developed a routine analytical procedure for the pyrolytic oils which utilizes a DuPont Model 21-490 GC-mass spectrometer interfaced to a DuPont Model 21-094B data acquisition system. The gas chromatograph used was the Varian 1440 and GC conditions were the same described in previous GC/MS runs. The reconstructed gas chromatogram is shown in Figure 12 for the oil obtained from Blue IV pilot plant condenser No. 1. Mass spectra are shown in Figures 13-22. Mass spectral assignments are shown in Table 11. Reconstructed gas chromatograms for oil from condenser No. 2, condenser No. 3, the draft fan and demister are shown in Figures 23,24,25, and 26 respectively. Mass spectral assignments are shown in Tables 12,13,14, and 15 respectively.

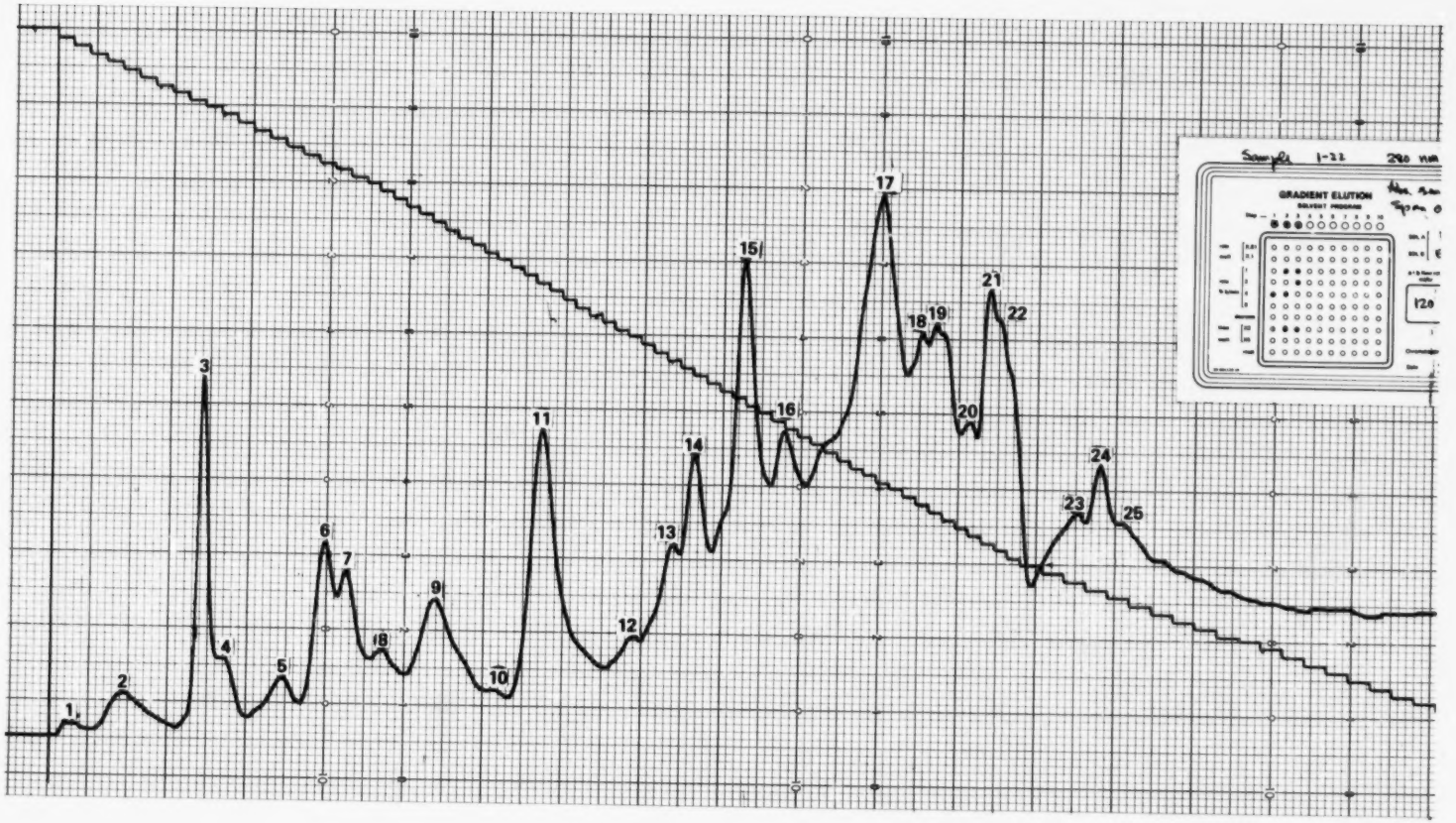

Figure 11. Liquid Chromatogram of Pine Condenser Oil Column Eluate at 280 nm.

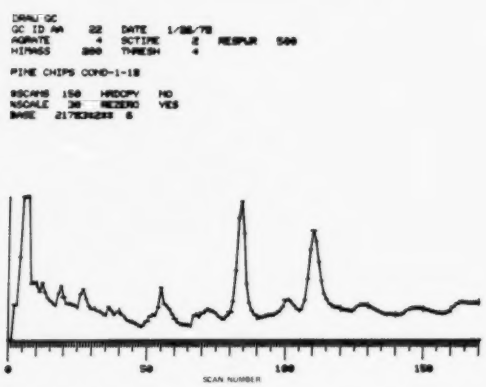

Figure 12. Reconstructed Gas Chromatogram of Pine Oil from Condenser No. 1.

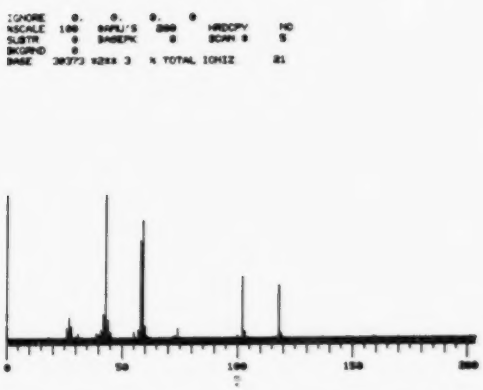

Figure 13. Mass Spectral Scan No. 5 for Pine Oil from Condenser No. 1.

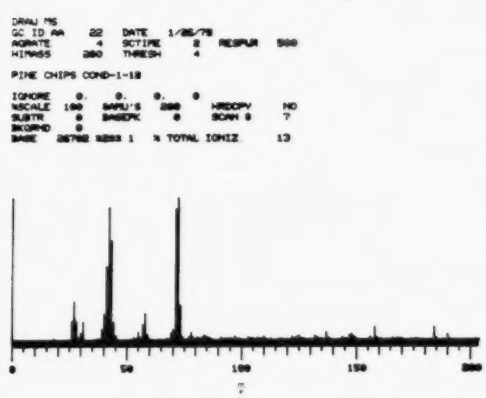

Figure 14. Mass Spectral Scan No. 7 for Pine Oil from Condenser No. 1.

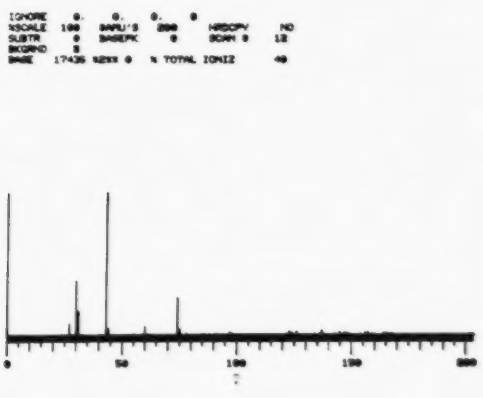

Figure 15. Mass Spectral Scan No. 12 for Pine Oil from Condenser No. 1.

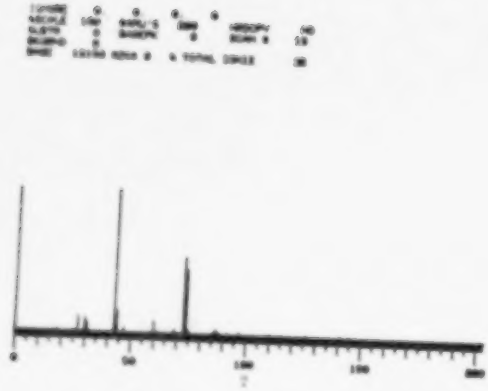

Figure 16. Mass Spectral Scan No. 19 for Pine Oil from Condenser No. 1.

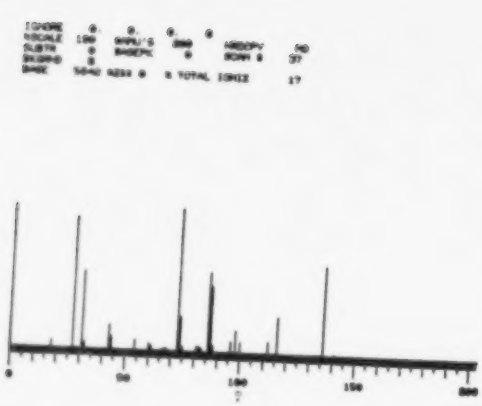

Figure 17. Mass Spectral Scan No. 37 for Pine Oil from Condenser No. 1.

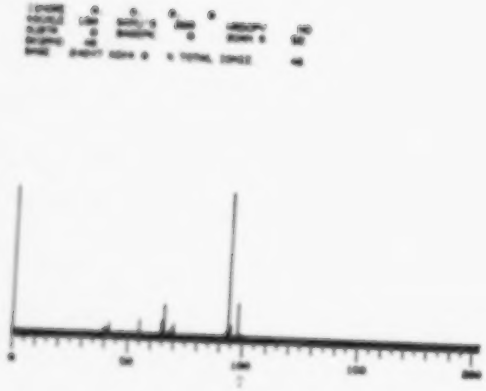

Figure 18. Mass Spectral Scan No. 52 for Pine Oil from Condenser No. 1.

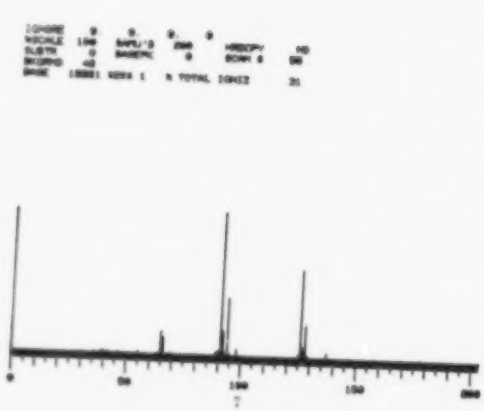

Figure 19. Mass Spectral Scan No. 55 for Pine Oil from Condenser No. 1.

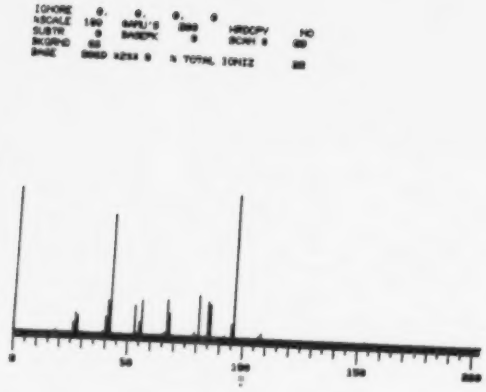

Figure 20. Mass Spectral Scan No. 69 for Pine Oil from Condenser No. 1.

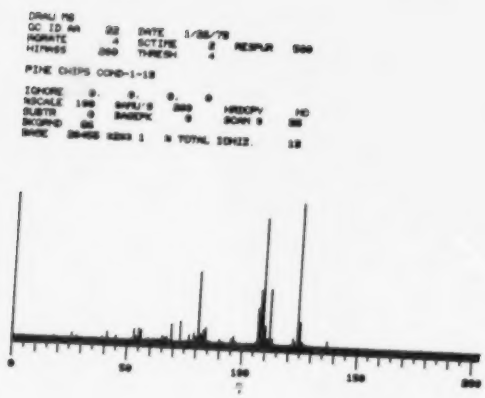

Figure 21. Mass Spectral Scan No. 85 for Pine Oil from Condenser No. 1.

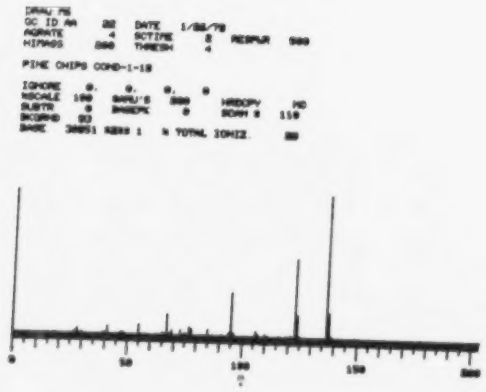

Figure 22. Mass Spectral Scan No. 110 for Pine Oil from Condenser No. 1.

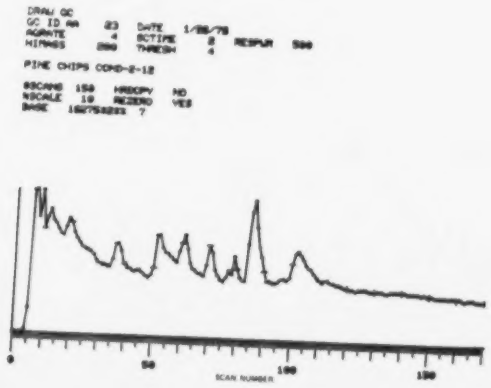

Figure 23. Reconstructed Gas Chromatogram of Pine Oil from Condenser No. 2.

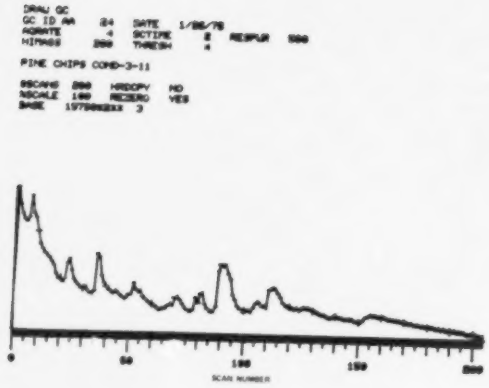

Figure 24. Reconstructed Gas Chromatogram of Pine Oil from Condenser No. 3.

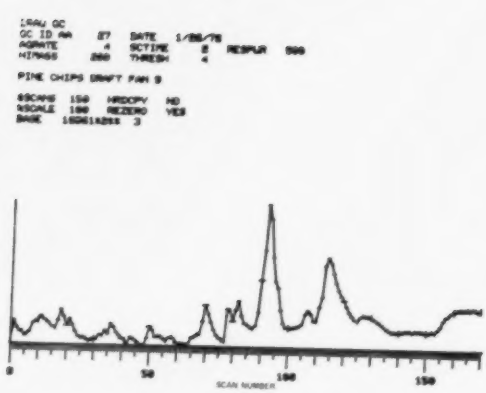

Figure 25. Reconstructed Gas Chromatogram of Pine Draft Fan Oil.

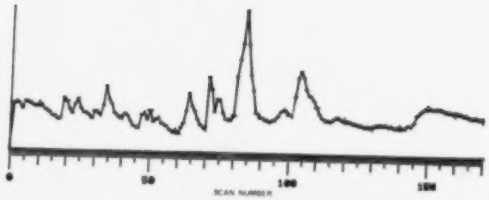

Figure 26. Reconstructed Gas Chromatogram of Pine Demister Oil.

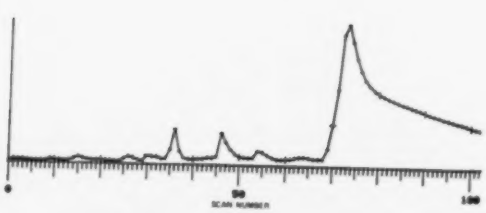

Figure 27. Reconstructed Gas Chromatogram of Hardwood Oil from Condenser No. 1.

TABLE 11. Results of Routine GC/MS/DS Analysis of Pine Condenser Oil #1

Scan No.	Components
5	Solvent
12-16	Isobutyl Alcohol, Acetic Acid
17	Unknown
19-21	Propionic Acid
27-31	Furfural, Furfuryl Alcohol
32-33	Furfural, Furfuryl Alcohol, Methylfuran
34-37	Heptanol, Methylfuran
38	Heptanol
50-53	Phenol
54-57	Phenol, Toluene
61,62	5-Methylfurfural, Phenol
68,69	Unknown
70-72	Cresol
73-77	Cresol, Heptaldehyde
78-80	Cresol
81-84	Guaiacol, Cresol
95-98	Dimethylphenol
101-104	Unknown
108-110	2-Methoxy-4-methylphenol
128	Anethole, Hydroxyacetophenone

TABLE 12. Results of Routine GC/MS/DS Analysis of Pine Condenser Oil #2

Scan No.	Components
5	Ethanol, Acetaldehyde
7	Unknown
9-10	Solvent
11	Acetic Acid, Unkown
12	Unknown
19	Isobutyl Alcohol
36	1-Butanol
53	Furfural, Furfuryl Alcohol
62	5-Methylfurfural
68,69	Phenol, Octanol
72-76	Phenol, Hydroquinone and/or Phenol
79,80	Cresol
85-88	Guaiacol, Cresol
100-108	2-Methoxy-4-methylphenol

TABLE 13. Results of Routine GC/MS/DS Analysis of Pine Condenser Oil #3

Scan No.	Components
1-4	Acetic Acid, Ethanol, Acetaldehyde
6	Toluene, Acetic Acid, Ethanol, Acetaldehyde
7	Isobutyl Alcohol
23	1-Butanol
37-43	Furfural, Furfuryl Alcohol
56	5-Methylfurfural
66	Phenol
72	Phenol, Hydroquinone and/or Resorcinol
82-88	Cresols
90,91	Guaiacol, Cresol
110	2-Methoxy-4-methylphenol
126	Anethole, Hydroxyacetophenone

TABLE 14. Results of Routine GC/MS/DS Analysis of Pine Draft Fan Oil

Scan No.	Components
13	Isobutyl Alcohol
21	1-Butanol
36	Furfural, Furfuryl Alcohol
51	Unknown
54-58	Unknown
65-68	Phenol
69,70	Phenol, Octanol
71-77	5-Methylfurfural, Phenol
81-85	Cresols
90	Guaiacol, Cresols
99-104	Guaiacol, Cresols, Dimethylphenol
107	Unknown
111-120	2-Methoxy-4-methylphenol
127	Anethole

TABLE 15. Results of Routine GC/MS/DS Analysis of Pine Demister Oil

Scan No.	Components
1	Acetic Acid, Ethanol
6-9	Isobutyl Alcohol

TABLE 15 (continued)

Scan No.	Components
24-26	1-Butanol
35,36	Furfural, Furfuryl Alcohol
41	Furfural, Furfuryl Alcohol, Methylfuran
51	5-Methylfurfural
60,63	Phenol
64	Phenol, Octanol
74-79	Cresols
82-92	Guaiacol,Cresol
93	Guaiacol Dimethylphenol
103-108	2-Methoxy-4-methylphenol
148	Anethole, Hydroxyacetophenone

Routine GC/MS/DS Analysis of Hardwood Pyrolytic Oils

We also analyzed Hardwood pyrolytic oil samples using the GC/MS/DS system. Reconstructed gas chromatograms for Hardwood condenser oils No. 1,2, and 3 are shown in Figures 27,28, and 29. Mass spectral assignments for the condenser oils are shown in Tables 16,17, and 18 respectively. Mass spectra for Hardwood condenser oil No. 3 are shown in Figures 30-37.

Reconstructed gas chromatograms for the Hardwood draft fan oil and demister oils are shown in Figures 38 and 39 respectively. The mass spectral assignments for the Hardwood draft fan oil and demister oils are shown in Tables 19 and 20 respectively.

TABLE 16. Results of Routine GC/MS/DS Analysis of Hardwood Condenser Oil #1

Scan No.	Components
15	Furfural, Furfuryl Alcohol
26	Phenol
32	Cresols
36	Guaiacol
46	2-Methoxy-4-methylphenol
54	2-Methoxy-4-ethylphenol
73	Unknown (MW 220)

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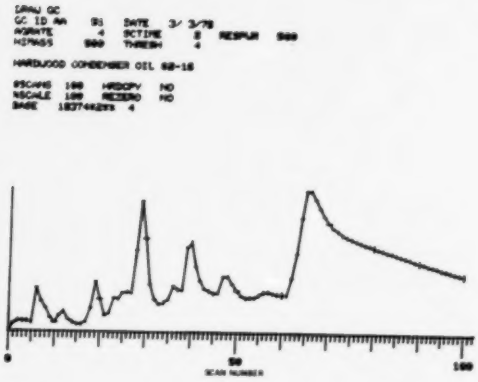

Figure 28. Reconstructed Gas Chromatogram of Hardwood Oil from Condenser No. 2.

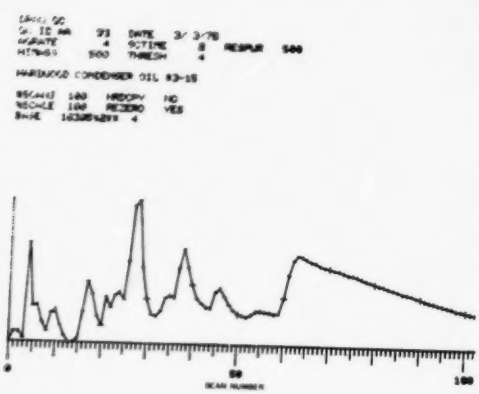

Figure 29. Reconstructed Gas Chromatogram of Hardwood Oil from Condenser No. 3.

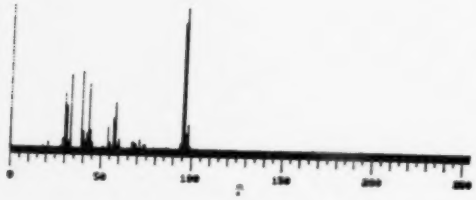

Figure 30. Mass Spectral Scan No. 4 for Hardwood Oil from Condenser No. 3.

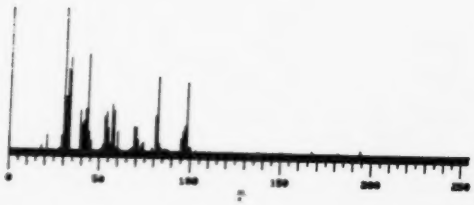

Figure 31. Mass Spectral Scan No. 6 for Hardwood Oil from Condenser No. 3.

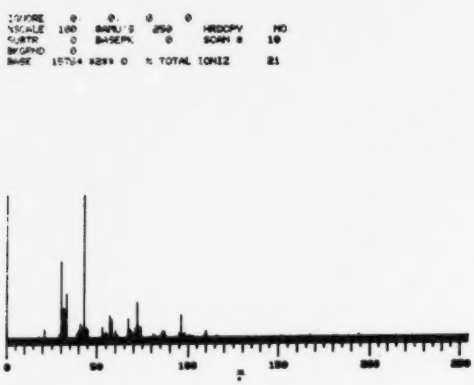

Figure 32. Mass Spectral Scan No. 10 for Hardwood Oil from Condenser No. 3.

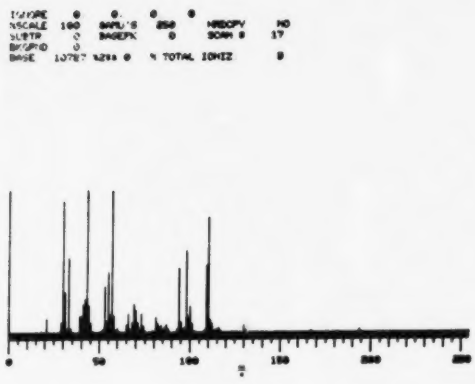

Figure 33. Mass Spectral Scan No. 17 for Hardwood Oil from Condenser No. 3.

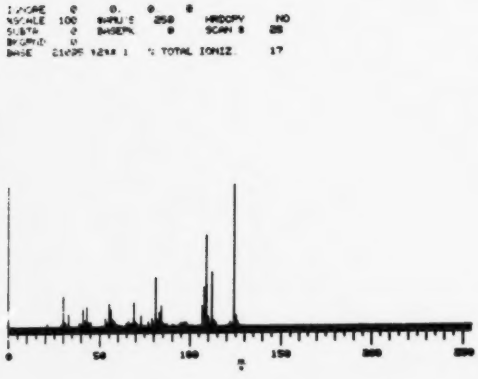

Figure 34. Mass Spectral Scan No. 28 for Hardwood Oil from Condenser No. 3.

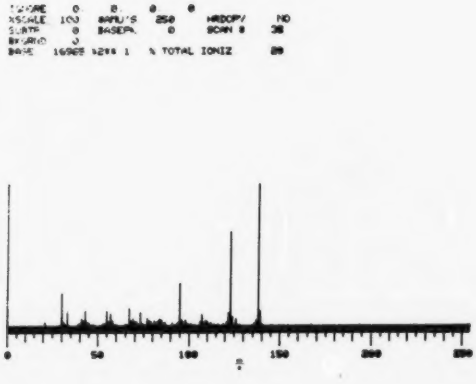

Figure 35. Mass Spectral Scan No. 38 for Hardwood Oil from Condenser No. 3.

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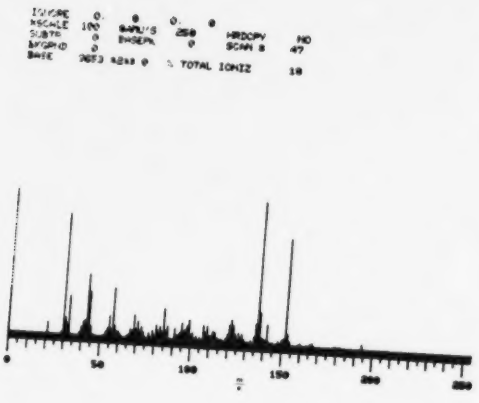


Figure 36. Mass Spectral Scan No. 47 for Hardwood Oil from Condenser No. 3.

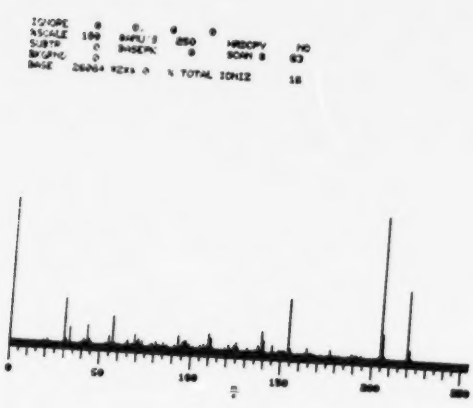


Figure 37. Mass Spectral Scan No. 63 for Hardwood Oil from Condenser No. 3.

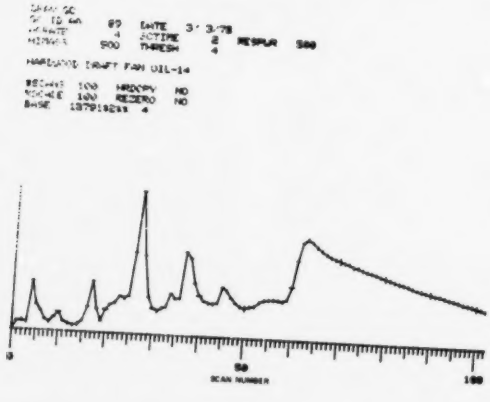


Figure 38. Reconstructed Gas Chromatogram of Hardwood Draft Fan Oil.

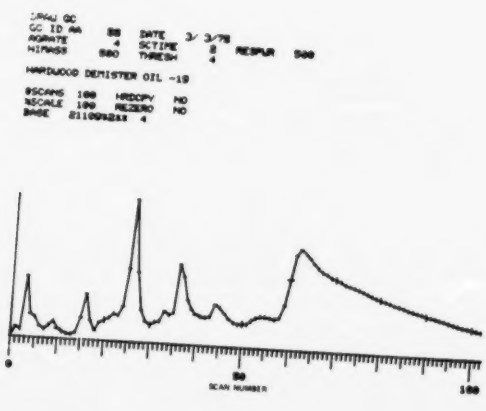


Figure 39. Reconstructed Gas Chromatogram of Hardwood Demister Oil.

TABLE 17. Results of Routine GC/MS/DS Analysis of Hardwood Condenser Oil #2

Scan No.	Components
8	Furfural, Furfuryl Alcohol, Acetone
12	Furfural
19	Phenol, 5-Methylfurfural
26	Cresols, Unknown
29	Guaiacol, Unknown
37	Veratrole, Naphthalene, Dimethoxyphenol
41	2-Methoxy-4-methylphenol
48	2-Methoxy-4-ethylphenol
57	2-Methoxy-4-propylphenol, Eugenol
65	Unknown (MW 220)

TABLE 18. Results of Routine GC/MS/DS Analysis of Hardwood Condenser Oil #3

4	Furfural
5	Furfural, Furfuryl Alcohol
6	Furfuryl Alcohol
10	Unknown
17	5-Methylfurfural, Phenol
21	Unknown
23	Cresol
27	Guaiacol, Unknown (MW 112), Cresol
35	Veratrole, Dimethylphenol, Unknown
38	2-Methoxy-4-methylphenol
46	2-Methoxy-4-ethylphenol
56	2-Methoxy-4-propylphenol, Eugenol
63	Unknown (MW 220)

TABLE 19. Results of Routine GC/MS/DS Analysis of Hardwood Draft Fan Oil

Scan No.	Components
4	Furfural
6	Furfural, Furfuryl Alcohol
10	Unknown

TABLE 19 (continued)

Scan No.	Components
17	5-Methylfurfural, Phenol
21	Unknown
23	Cresol
27	Guaiacol, Cresol, Unknown (MW 112)
34	Veratrole, Naphthalene, Methoxyphenol
37	2-Methoxy-4-methylphenol
46	2-Methoxy-4-ethylphenol
56	2-Methoxy-4-propylphenol, Eugenol
63	Unknown (MW 220)

TABLE 20. Results of Routine GC/MS/DS Analysis of Hardwood Demister Oil

Scan No.	Components
1	Acetic Acid, Furfural, 1-Butanol
3	Furfural
4	Furfural, Furfuryl Alcohol
9	Unknown
16	5-Methylfurfural, Phenol
21	Unknown
26	Guaiacol, Cresol, Unknown
33	Veratrole, Naphthalene, Methoxyphenol
37	2-Methoxy-4-methylphenol
45	2-Methoxy-4-ethylphenol
55	2-Methoxy-4-propylphenol, Eugenol
64	Unknown (MW 220)

Extractive Procedures for the Pyrolytic Oils

The condenser oil was separated into various chemical classes by using standard extractive procedures. The condenser oil (84g) was first extracted with water. Evaporation of the aqueous solution led to the isolation of a liquid (6.6g) which distilled in the range of 100-124°C This class should include sugars and low molecular weight compounds such as alcohols, aldehydes, ketones, and carboxylic acids.

The residue from aqueous extraction was treated with 5% sodium hydroxide solution. The insoluble fraction was extracted with diethyl

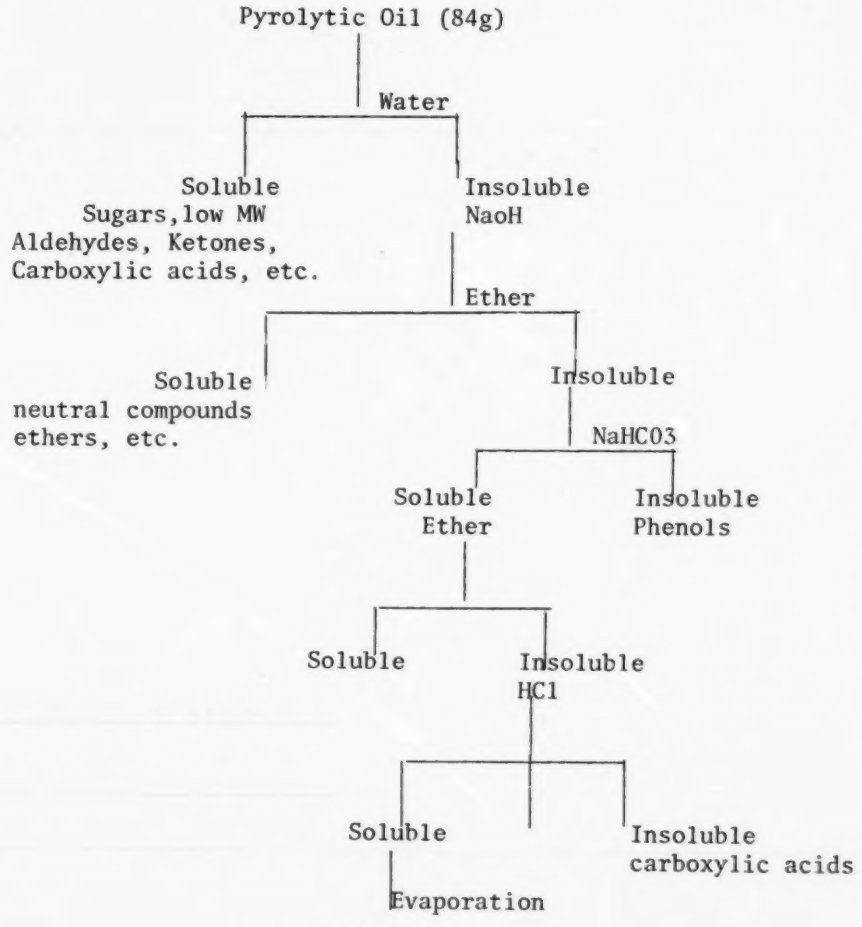
ether. The ether solution was evaporated and the residue distilled to yield 2.2g of a liquid. The compounds in this class should include miscellaneous neutral compounds and bases. Since no bases should be present in the pyrolytic oils, ethers, and higher molecular weight neutral compounds are included in this class.

The sodium hydroxide solution was treated with 5% sodium bicarbonate solution to yield an insoluble brown solid (10.4g). The addition of sodium bicarbonate solution results in the formation of insoluble weak acids such as phenols.

The combined sodium hydroxide and sodium bicarbonate solution was neutralized with HCl to form an insoluble solid (1.2g). This procedure should result in the isolation of strong acids such as carboxylic acids.

The solution was evaporated and 12.6g of a solid was obtained. The total recovery was thirty three grams (39%). The procedure is shown below.

CHEMICAL CLASS SEPARATION OF THE PYROLYTIC OILS



Preparation of Phenol-Formaldehyde Resins

Other investigators have used the tar[16] and creosote[17] fraction from wood pyrolysis for the preparation of phenol-formaldehyde resins. In our work, condenser oil (84g) was first extracted with 100ml. of distilled water. After discarding the aqueous layer, the isoluble layer was extracted with 25ml. of 1.5 N $NaHCO_3$. The aqueous layer was discarded and the insoluble layer was treated with 25ml. of 2.5N NaOH. To this layer was added 5% HCl to neutralization. The phenols (4.1g) were isolated by extraction of the neutralized solution with diethyl ether.

The phenols (35g) were condensed with 42g of formalin in 4g of water and 2g barium hydroxide. A low molecular weight reosole (7.9g) was formed which on additional heating formed a crosslinked resin.

Evaluation of Pyrolytic Oils as a Feedstock for the Recovery and Production of Chemicals

The potential of the pyrolytic oils as a source of chemicals is excellent. The following table contains a listing of valuable chemicals present in the pyrolytic oils and their prices as listed in the August 21, 1978 issue of CHEMICAL MARKETING REPORTER[18].

TABLE 21. Current Prices of Chemicals Present in the Pyrolytic Oils

Chemical	Price $ per lb.	Comments
Acetaldehyde	0.20	99%
Acetic Acid	0.18	technical grade
Acetone	0.17	
n-Butyl Alcohol	0.21	fermentation grade
sec-Butyl Alcohol	0.23	synthetic
Butyric Acid	0.325	
m-Cresol	0.98	95-98%
m,p-Cresol	0.44	90%
o-Cresol	0.50	30.5°C m.p.
Ethyl Alcohol	1.12	190 proof
Eugenol	4.25	USP
Furfural	0.515	
Furfuryl Alcohol	0.54	
Guaiacol	2.60	technical grade
Hexyl Alcohol	0.24	mixed isomers
Hydroquinone	1.54	technical grade
Isobutyl Alcohol	0.19	
Isoeugenol	6.85	
Methanol	0.44	synthetic

TABLE 21 (continued)

Chemical	Price $ per lb.	Comments
p-Methylnaphthalene	0.90	
Naphthalene	0.12	crude
1-Octanol	0.40	
Phenol	0.19	synthetic
Isobutyric Acid	0.75	

Among the particularly valuable chemicals present in the pyrolytic oils are Eugenol, Isoeugenol, Guaiacol, hydroquinone and the cresols which are present in the Creosote fraction. The creosote fraction may be removed from the pyrolytic oil by (1) extracting with water and discarding the aqueous layer, (2) extracting with 1.5N $NaHCO_3$ to remove the carboxylic acids and (3) extracting with 2.5N NaOH followed by neutralization with 5% HCl solution. The capillary gas chromatogram of the Creosote fraction is shown in Figure 40. The peaks at retention times of 16.4 (7.0gc%), 17.9 (5.7gc%), 18.0 (3.3gc%) 19.0 (10.0gc% 21.0 (14.gc%), 24.7 (4.0gc%), and 28.4 (3.9gc%) min. are Guaiacol, o-cresol, m-and p-cresol, 2-methoxy-4-methylphenol, Eugenol, and Isoeugenol, respectively.

Stabilization Studies

Figure 41A shows the capillary gas chromatogram (June 16, 1978) of the pyrolytic oil obtained from the Georgia Tech Blue IV unit of June 14, 1978. The chromatogram of the aged sample was run on March 5, 1979 and is shown in Figure 41B. Peak 64 completely disappeared and peak 79 decreased significantly in area over that period. Peak 79 is Isoeugenol and we have demonstrated that peak 64 is 4-hydroxy-3-methoxystyrene by synthesis from 4-hydroxy-3-methoxy cinnamic acid. Under the low pH conditions of the pyrolytic oils both olefins would be expected to polymerize. The retention time of the authenic 4-hydroxy-3-methoxystyrene sample was found to be identical to that of peak no 64.

Figure 41C is the capillary gas chromatogram of hydrogenated Blue IV oil. Peak 64 (4-hydroxy-3-methoxystyrene) has disappeared and peaks 69 and 79 (eugenol and isoeugenol) have decreased in area. Peaks 58 and 70 (2-methoxy-4-ethylphenol and 2-methoxy-4-propylphenol) have increased in area. Hydrogenation of Blue IV oil resulted in the conversion of 4-hydroxy-3-methoxystyrene to 2-methoxy-4-ethylphenol and eugenol and isoeugenol to 2-methoxy-4-propylphenol. The oil was hydrogenated on July 12, 1978 and the gas chromatogram was run on July 13, 1978. Figure 41D is the capillary gas chromatogram of hydrogenated Blue IV oil on March 5, 1979. Once again, peak 79 (isoeugenol) has decreased in area.

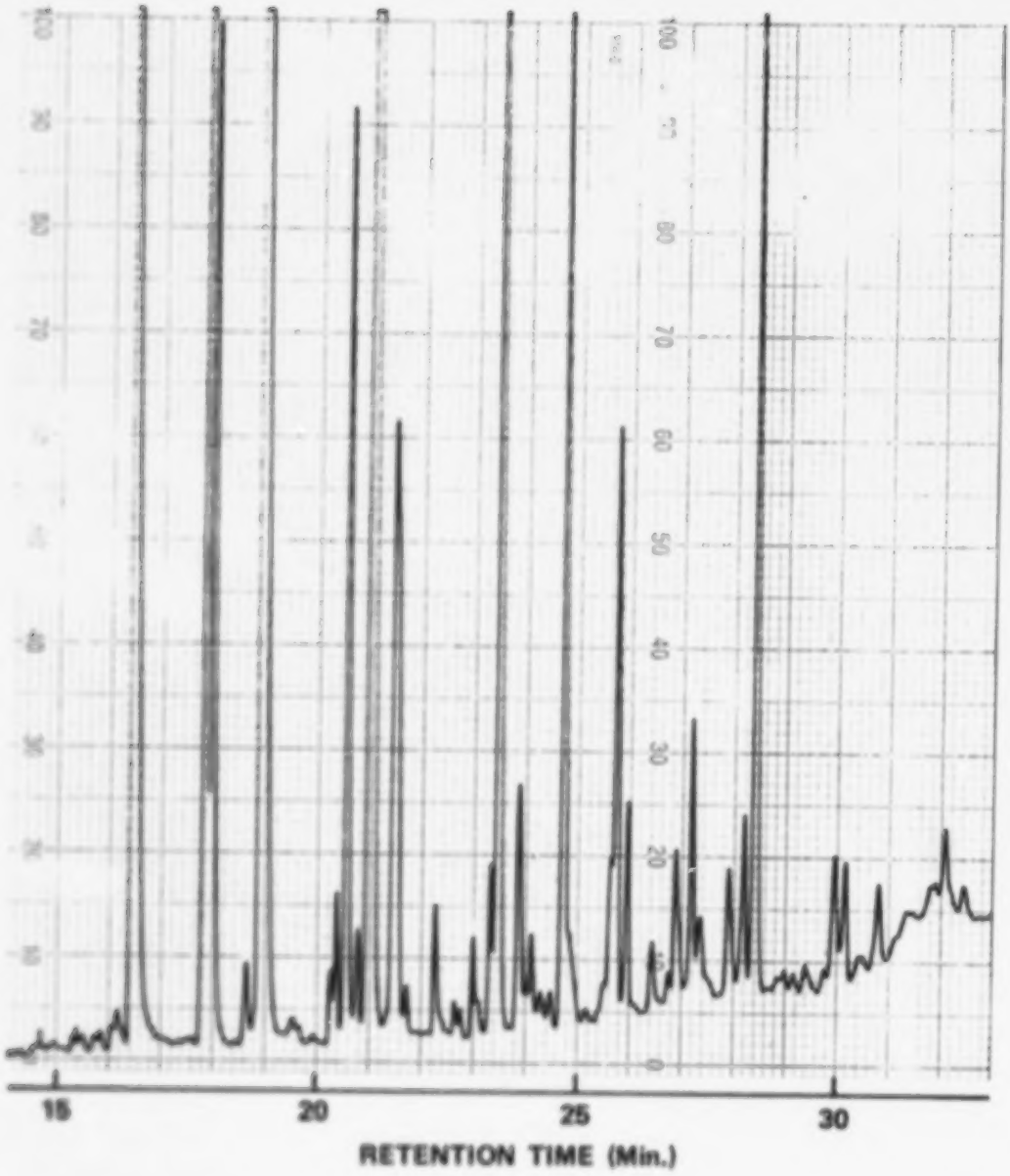


Figure 40. Capillary Gas Chromatogram of Phenolic Extract.

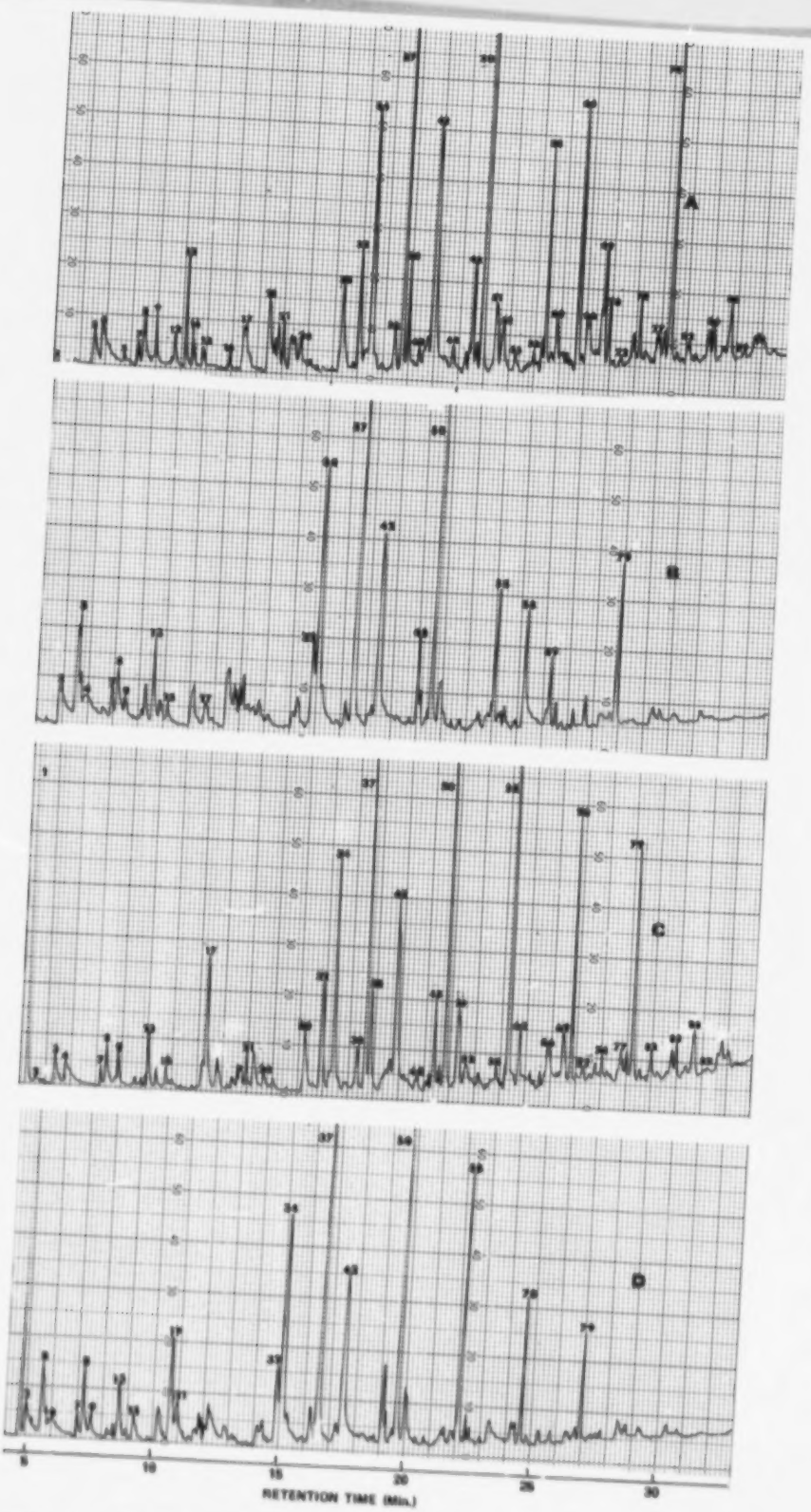


Figure 41. Capillary Gas Chromatogram of Blue IV Oil. A 6/16/78), B (3/5/79), C (hydrogenated - 7/13/78), D (hydrogenated - 3/15/79).

Over the nine month period a 20% v/v Blue IV oil in m-cresol sample showed an increase in relative viscosity at 35°C of 1.38 on June 14, 1978 to 2.37 on March 22, 1979. A hydrogenated 20% v/v Blue IV oil in m-cresol sample showed an increase in relative viscosity of 1.35 on July 12, 1978 to 1.64 on March 21, 1979. The hydrogenated oil however, did contain more low molecular weight alcohols because of hydrogenation and some solvent may still have been present.

The observation that isoeugenol and 4-hydroxy-3-methoxystyrene peaks disappear on aging substantiates our suggestion that cationic chain-reaction polymerization or oligomerization is responsible for the substantial increases in viscosity of the pyrolytic oils on aging.

Paired-Ion Chromatography

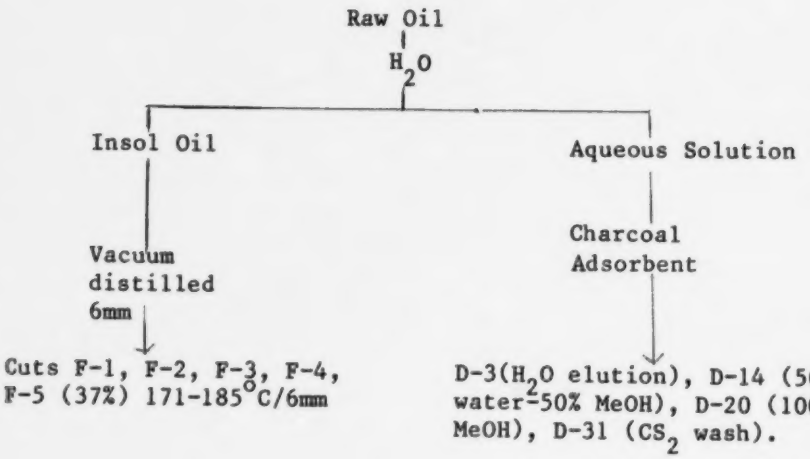
Paired-ion chromatography of the pyrolytic oil conducted at 280nm using a 25cm long MCH-10 column produced good chromatograms with moderate resolution and a marked decrease in the retention times of component peaks. Reagent B-5 (Waters Associates) was used for the preparation of paired-ion solvents. Solvent A was prepared by the addition of PIC Reagent B-5 (pentane sulfonic acid) to degassed destilled water. Solvent B was prepared by the addition of PIC Reagent B-5 to a 50/50 mixture of 2-propanol and acetontrile. Unsuccessful attempts were made to improve the resolution of the chromatograms by decreasing the rate of introduction of solvent B in the solvent program, but no substantial improvement resulted. The chromatograms produced with the paired-ion reagent were among the better chromatograms obtained for the pyrolytic oils however reproducibility was poor.

Routine Analysis of Samples from Extraction Studies

Two approaches were used for routine analysis of the pyrolytic oils. The approaches were capillary chromatography and coupled gas chromatography-mass spectrometry. Knight and co-workers at the Georgia Institute of Technology Engineering Experiment Station obtained samples by solvent extraction that may be divided into four general categories: 1) aqueous extract; 2) organic solvent (MiBK,$CHCl_3$) extract; 3) insoluble oil; and 4) volatiles.

The aqueous extracts were derivatized by Hydroxsil reagent (2 parts of hexamethlydisilazane, 1 part of trimethylchlorosilane and 10 parts of pyridine). The capillary gas chromatograph and gc-mass spectrometric runs were made on the aqueous extracts, silylated aqueous extracts, the organic solvent extracts, insoluble oils and volatiles as received, after filtering.

The samples analyzed and their origins are as follows:


Raw Oil
H_2O
Insol Oil
Aqueous Solution
Vacuum distilled 6mm
Charcoal Adsorbent
Cuts F-1, F-2, F-3, F-4, F-5 (37%) 171-185°C/6mm
D-3(H_2O elution), D-14 (50% water-50% MeOH), D-20 (100% MeOH), D-31 (CS_2 wash).

E-5 Raw Oil	% Solids
Aqueous Phase	100
MiBK Organic Phase	100 (no MiBK)

E-6 Raw Oil	% Solids
Aqueous Phase	100
MiBK Extract	100
Insoluble Oil	74
Volatiles	11 (organic volatiles in H_2O)

E-7 Vacuum Stripped Oil	% Solids
Aqueous Phase	100
MiBK Extract	100
Insoluble Oil	77
Volatiles	31 (organic volatiles in H_2O)

E-8 Vacuum Stripped Oil	% Solids
Aqueous Phase	≃20 (80% MiBK-H_2O)
MiBK Extract	≃40 (60% MiBK-H_2O)

Water Extraction Only

I-1A First Aqueous Extract
I-2A Second Aqueous Extract
I-3A Third Aqueous Extract
I-OR Water Insoluble Organic

Capillary Gas Chromatography of Samples from Extraction Studies

Originally capillary gas chromatography was performed on a Varian 3740 capillary gas chromatography under the following conditions: A 30 meter Supelco 2-3700 glass capillary grade AA SP 2100 column (internal diameter ca. 0.25mm), oven temperature program 40°C-250°C at 5°C per min. He flow rate - 1.0ml/min. The chromatograph has operated in the splitless mode. The splitter (set at a split ratio of 250:1) was generally turned off after 5 minutes. Later on in the project we discovered the availability of the CP Sil-5 glass WCOT columns from the Chrompack Co. CP Sil-5 is a non-polar polydimethylsiloxane like SE-30, OV-1, OV-101 and SP-2100. However it is stable on glass surfaces up to 325°C for isothermal analysis and 350°C for temperature programming. We obtained a 25m x 0.50mm CP Sil-5 glass WCOT column which was used to analyze the pyrolytic oils under the following conditions: He flow rate - 1.0ml/min., oven temperature program 40°C -325°C at 5°C per min. The retention times were much less on the CP Sil-5 column than on the SP 2100 column (e.g. Phenol SP 2100 - 15.0 min., CP Sil-5 -5.5 min.). As a result, we were able to discern the presence of much higher boiling components on the CP Sil-5 column (e.g. 1,8,9-trihydroxyanthracene, with a melting point of 178-180°C, elutes at a retention time of 37.7 min.).

The capillary chromatograms of the aqueous extracts were similar in that peaks characteristic of phenols, dihydroxybenzenes, and low molecular weight aldehydes, alcohols and acids were present. Components identified included acetic acid, phenol, furfural, o-cresol, Guaiacol, 2-methoxy-4-methylphenol, m-methoxyphenol, Eugenol, 2-methoxy-4-propylphenol, cis-and trans-Isoeugenol, 1-octanol, catechol and resorcinol. An interesting peak appeared at a retention time of 21.2 min. in the CP Sil-5 chromatogram of D-3 (Figure 42). Silylated D-20 had peaks at retention times as great as 23 minutes (silylated phloroglucinol appears at 22.6 min.). D-31 had a peak at 21.2 min. E-5 aqueous (Figure 43), E-6 aqueous, E-7 aqueous, and E-8 aqueous contained more low molecular weight alcohols and aldehydes than the D-series which contained the usual phenols, and a wide, interestingly poorly resolved peak at about 19 min. to 23 or 24 min. That peak may represent a highly hydroxylated material (possibly a sugar) which interacts strongly with -OH groups on the column. I-1A (Figure 44) contained the usual alcohols, aldehydes and phenols in addition to the wide collection of unresolved peaks at retention times of 21 to 24 min. I-2A (Figure 45) contains in addition to the usual alcohols, aldehydes and phenols, unidentified higher boiling components at retention times greater than 17 min. The capillary chromatogram of silylated I-2A (Figure 46) shows components with retention times as high as 44 min. I-3A (Figure 47) contained few peaks in addition to solvent and furfural. Silylated I-3A contained additional peaks at high retention times. Assignments for peaks in Figures 42-47 appear in Table 22.

TABLE 22. Results of Capillary Gas Chromatography of D-3, E-5 Aqueous, I-1A, I-2A, Silylated I-2A, and I-3A Aqueous Fraction.*

Component	Sample and Retention Time (Min)					
	D-3	E-5 Aqueous	I-1A	I-2A	Silylated I-2A	I-3A
Furfural	1.8	3.0	2.0	2.3	2.1	2.2
Phenol	5.3	6.1	5.1	5.3	5.7	5.3
o-Cresol	7.1	7.8	6.8	7.1	7.5	7.1
Guaiacol	7.6	8.2	7.4	7.6	8.0	7.7
2-Methoxy-4-methylphenol	10.6	11.2	10.2	10.1	10.9	10.6
Eugenol	14.9	15.7		15.2	15.3	
2-Methoxy-4-propylphenol		16.1		15.5	15.6	
cis-Isoeugenol		16.4		16.9	16.6	
trans-Isoeugenol				17.2	17.6	

*Analysis performed on CP Sil-5 Column

The capillary gas chromatograms of the organic extracts showed primarily the presence of phenol, o-cresol, m- and p-cresol, Guaiacol, 2-methoxy-4-methylphenol, 2-methoxy-4-ethylphenol, Isoeugenol and Eugenol. These assignments were confirmed by gc-mass spectrometry. One baffling peak remains unassigned. The peak appears at 38.4 min. in E-5 MiBK (Figure 48) and E-8 MiBK. The assignments for Figure 48 appear in Table 23.

The capillary gas chromatograms of the insoluble oil fractions contained peaks characteristic of furfural, o-cresol, m- and p-cresol, phenol, Guaiacol, 2-methoxy-4-methylphenol, m-methoxyphenol, 2-methoxy-4-ethylphenol, Eugenol, 2-methoxy-4-propylphenol, Isoeugenol, and higher boiling components which were not identifed. F-1 (Figure 49) did not contain the higher boiling components. As would be expected, the fraction of higher boiling components increased in the series F-2 (Figure 50), F-3, F-4 (Figure 51) and F-5 (Figure 52). The capillary gas chromatogram of I-OR is shown in Figure 53. Capillary gas chromatograms for E-6 and E-7 insoluble oils appear in Figures 54 and 55. The assignments for Figures 49-55 appear in Table 24.

The capillary gas chromatograms of E-6 volatiles (Figures 56) and E-7 volatiles (Figures 57) contain acetic acid as the main component. Other components present in E-7 volatiles included butanol, isomeric pentanols, isomeric heptanols, furfural, furfuryl alcohol, o-cresol, Guaiacol, and 2-methoxy-4-methylphenol. The assignments for Figures 54 and 55 appear in Table 25.

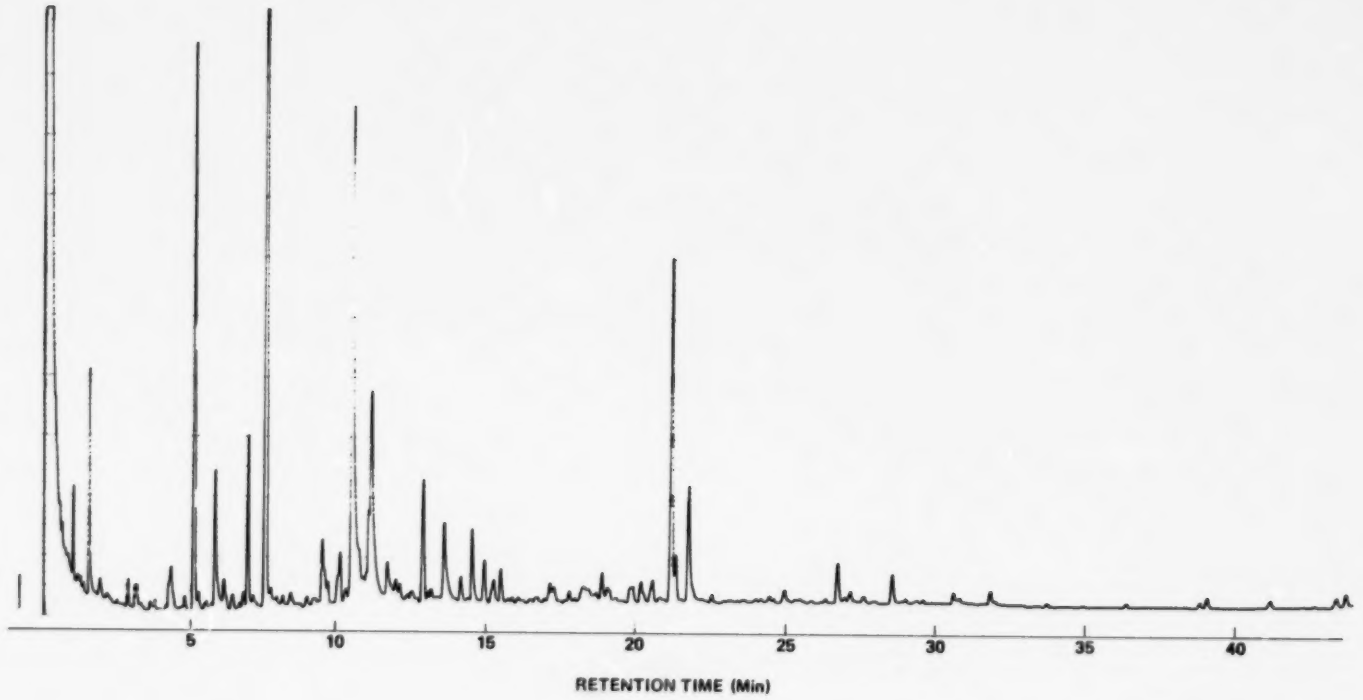


Figure 42. Capillary Gas Chromatogram of D-3 Aqueous Fraction.

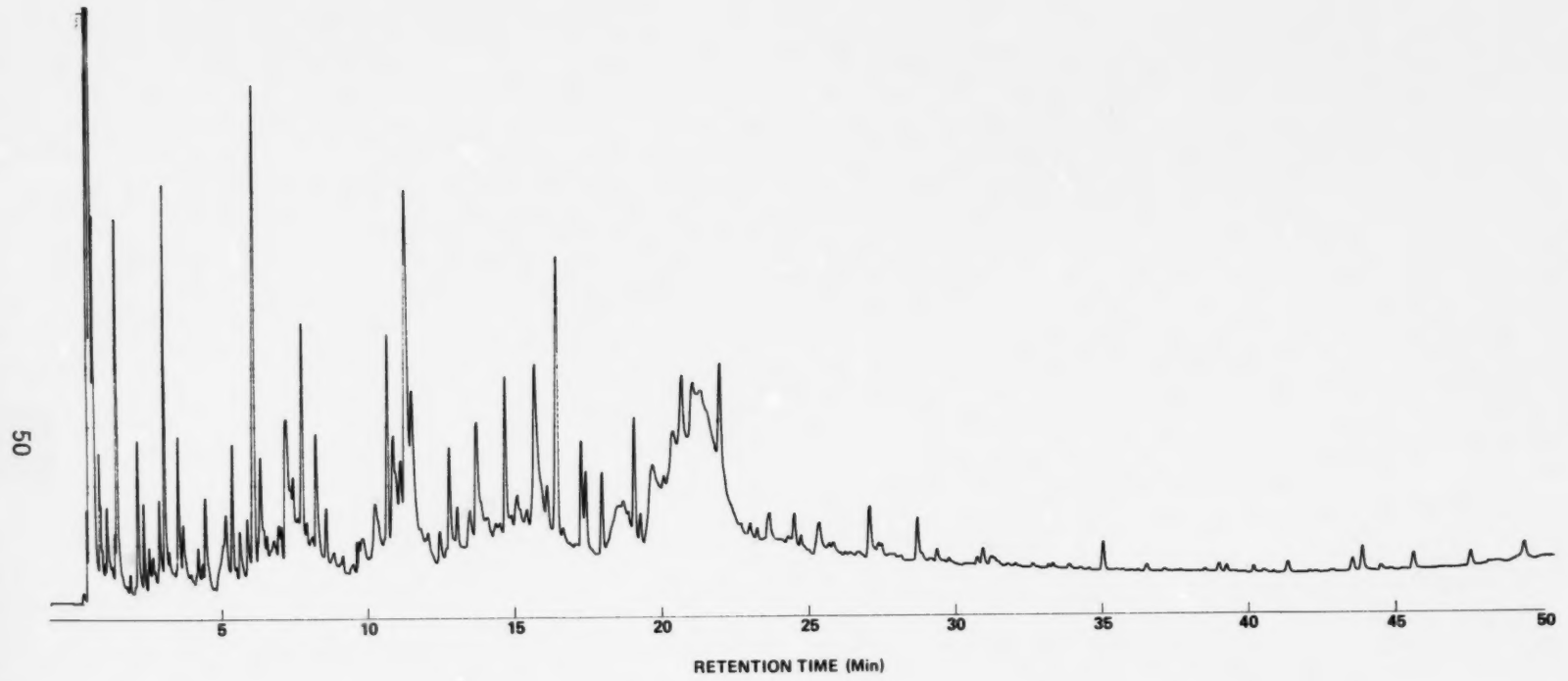


Figure 43. Capillary Gas Chromatogram of E-5 Aqueous Fraction.

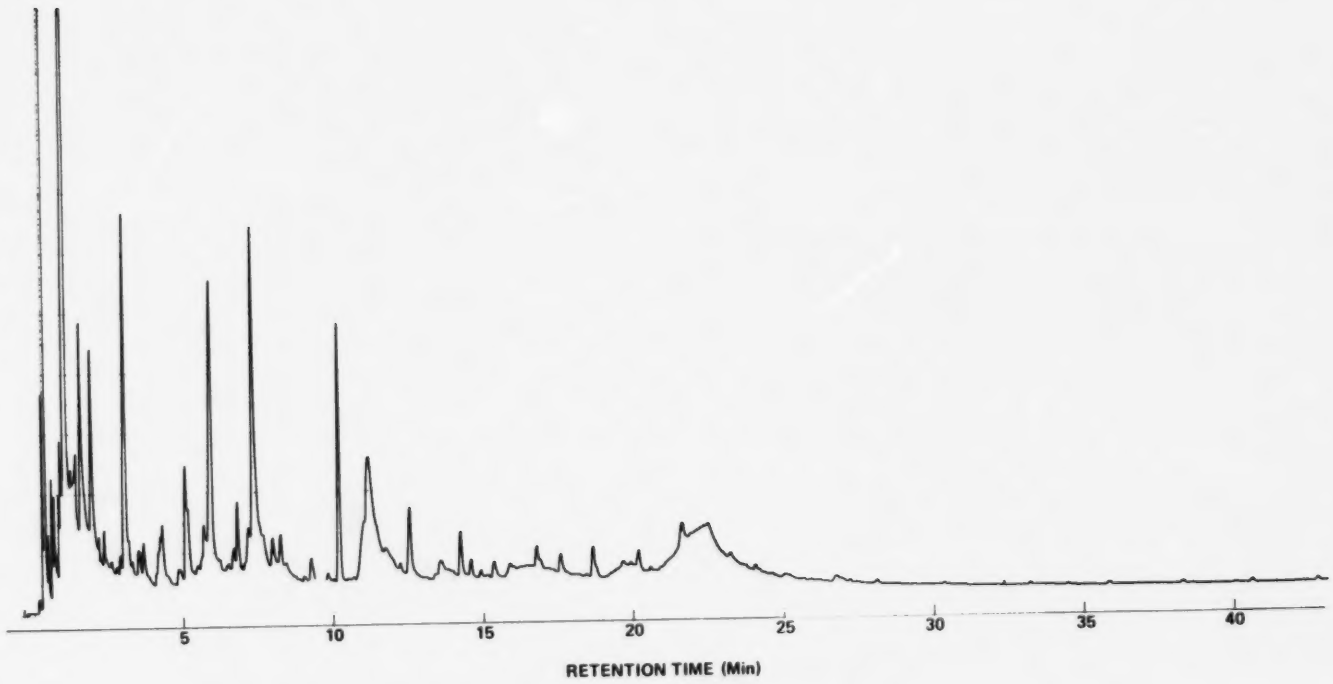


Figure 44. Capillary Gas Chromatogram of I-1A Aqueous Fraction.

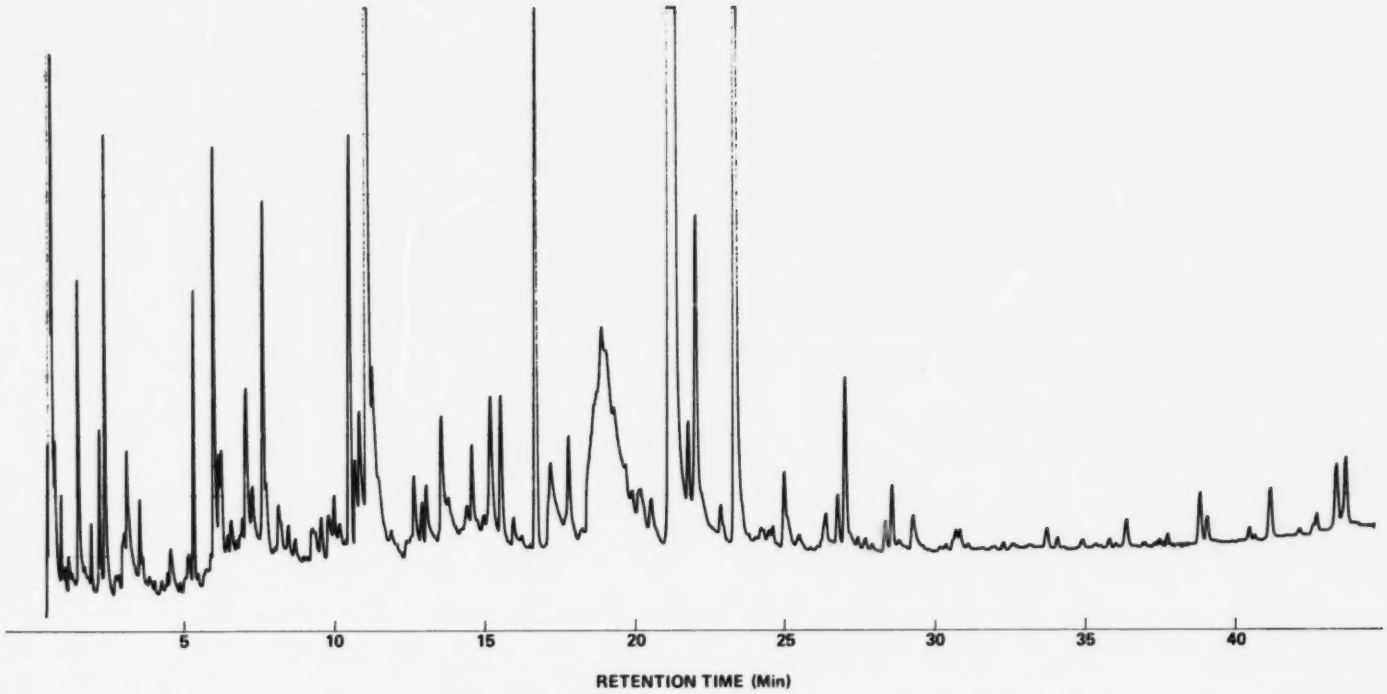


Figure 45. Capillary Gas Chromatogram of I-2A Aqueous Fraction.

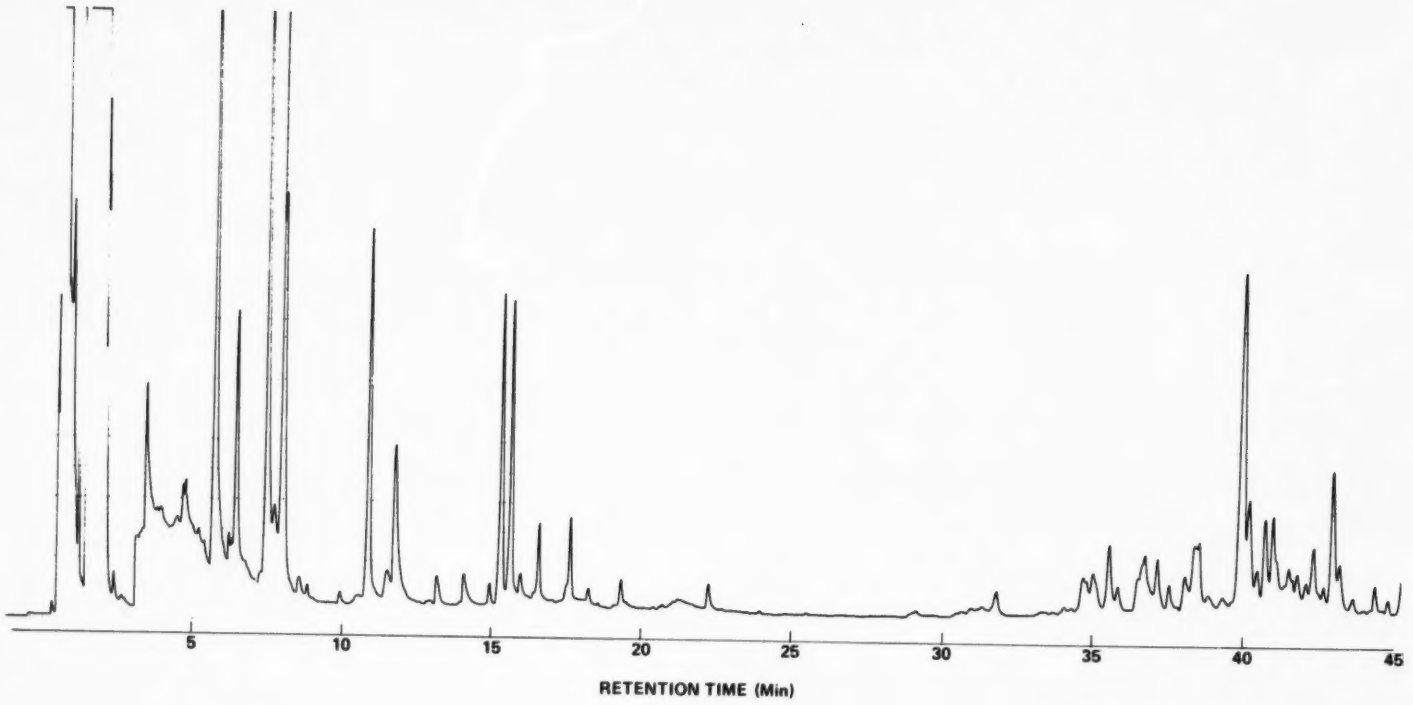


Figure 46. Capillary Gas Chromatogram of Silylated I-2A Aqueous Fraction.

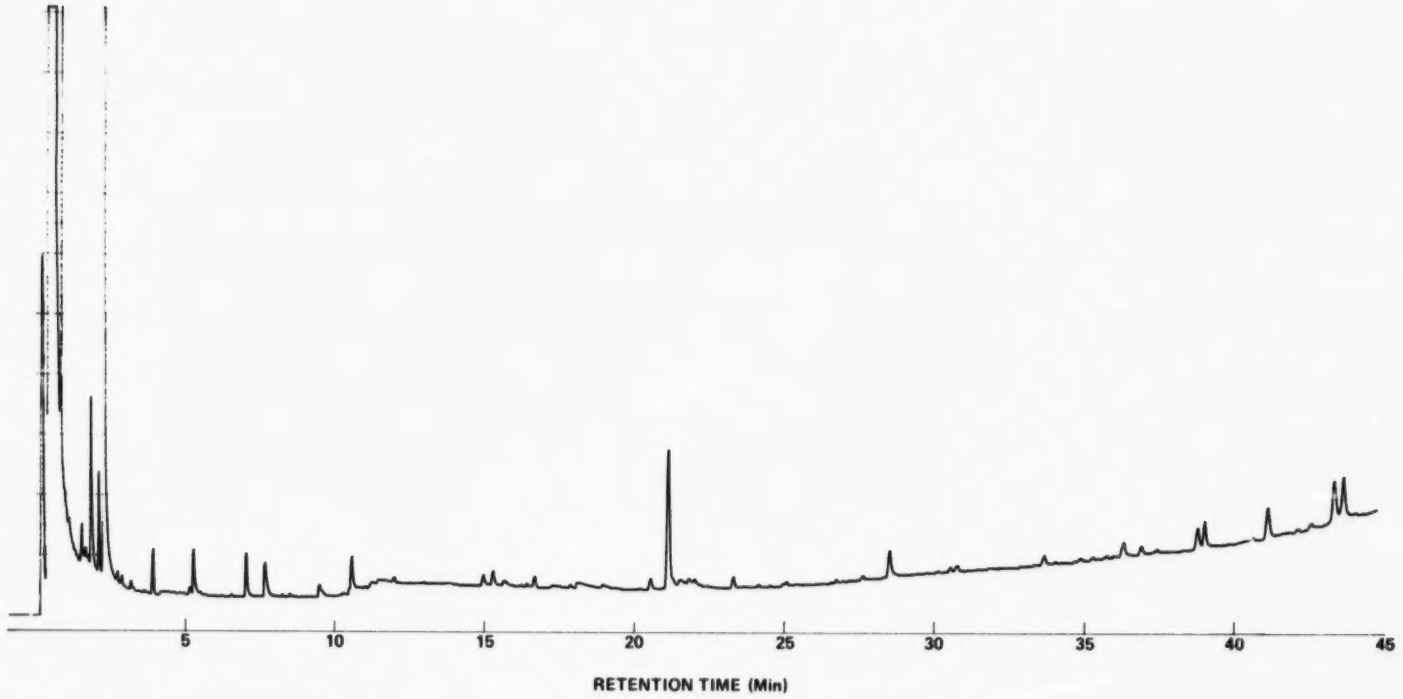


Figure 47. Capillary Gas Chromatogram of I-3A Aqueous Fraction.

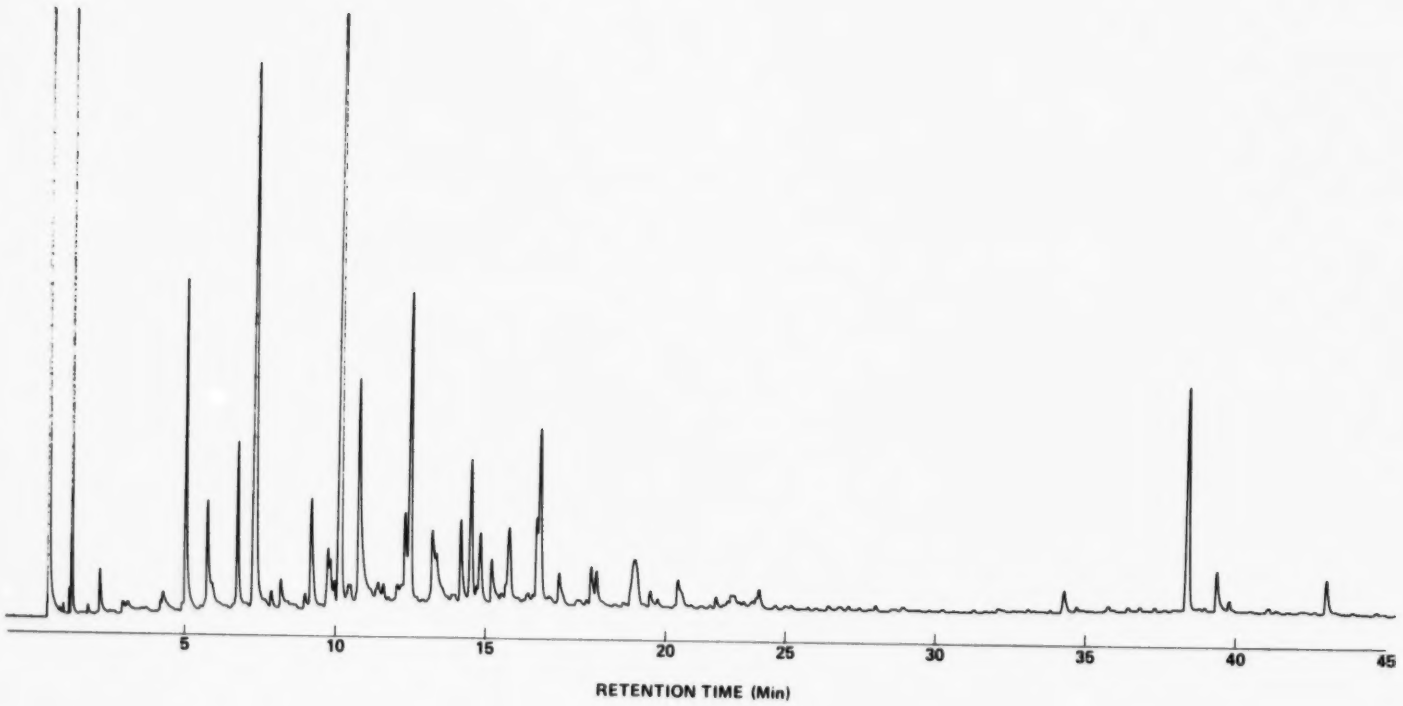


Figure 48. Capillary Gas Chromatogram of E-5 MIBK Extract.

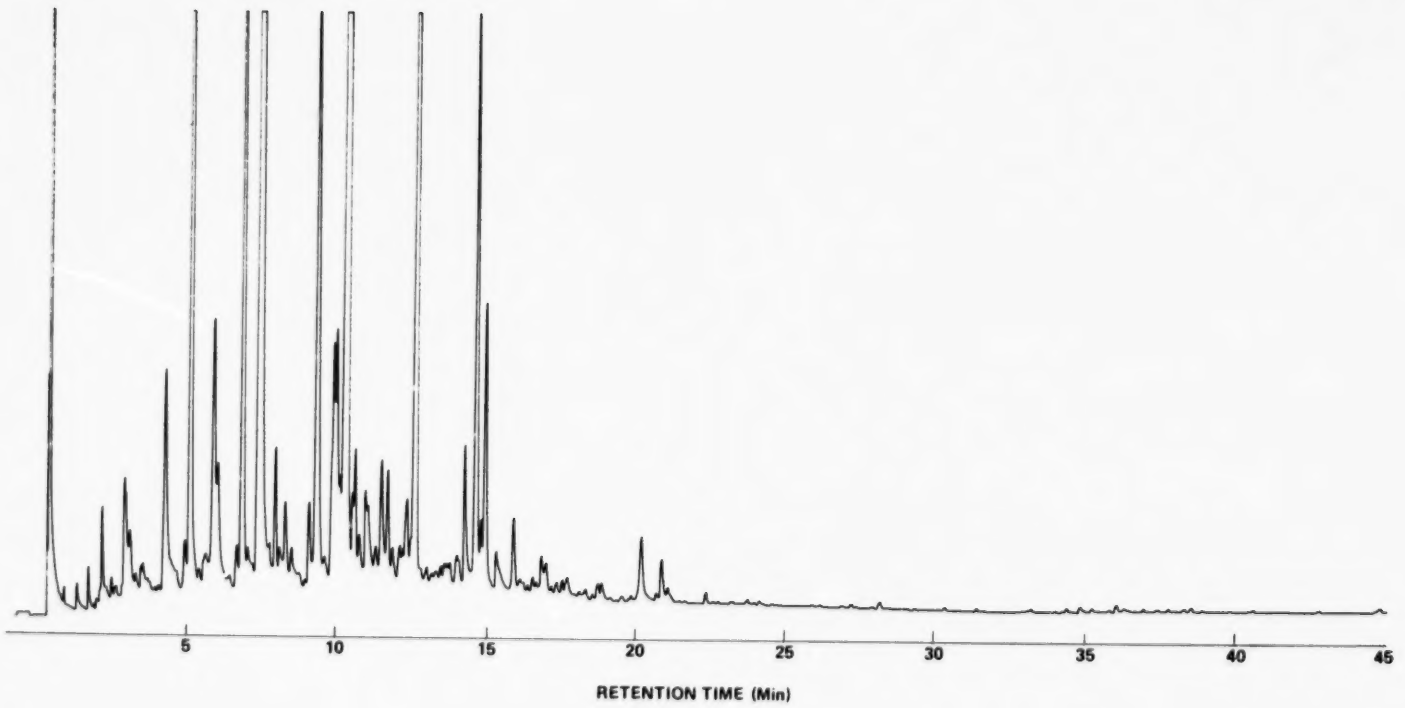


Figure 49. Capillary Gas Chromatogram of Vacuum Distilled Insoluble Oil Cut F-1.

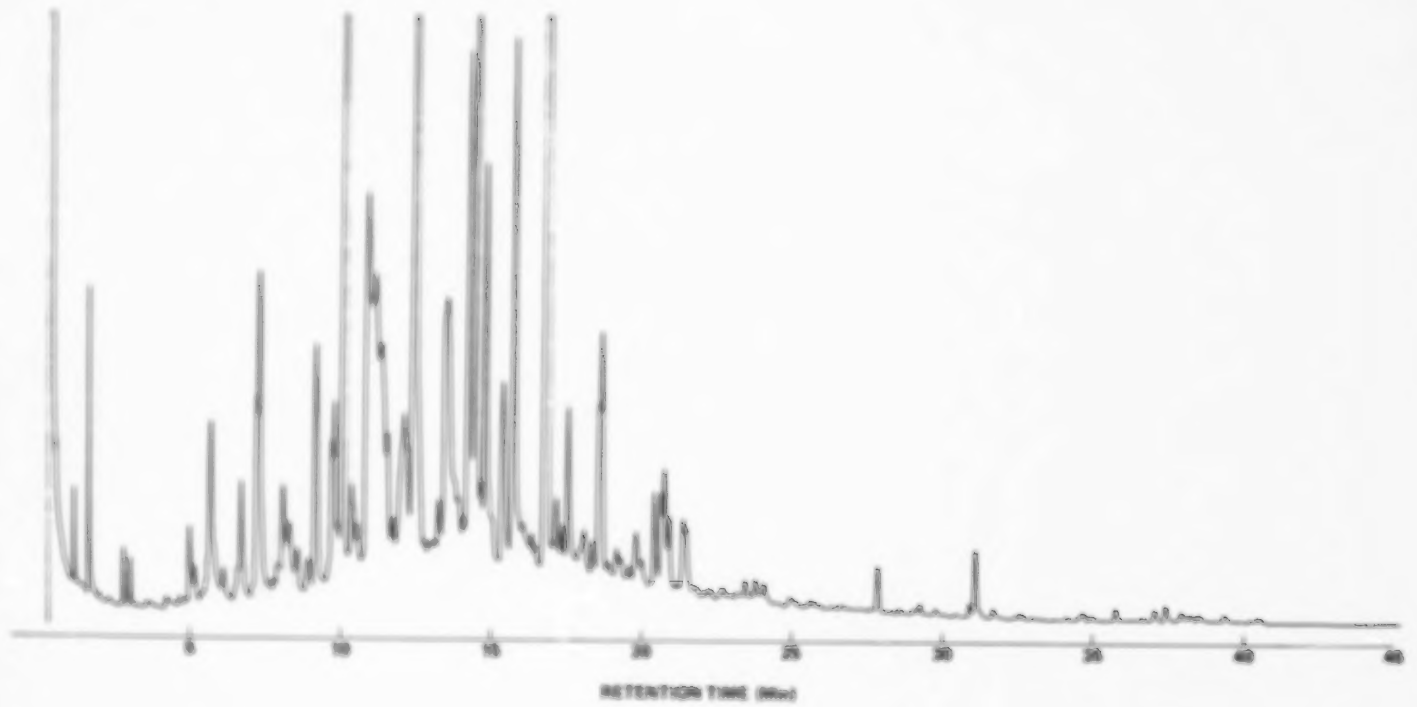


Figure 30. Capillary Gas Chromatogram of Vacuum Distilled Insoluble Oil Cut F-2.

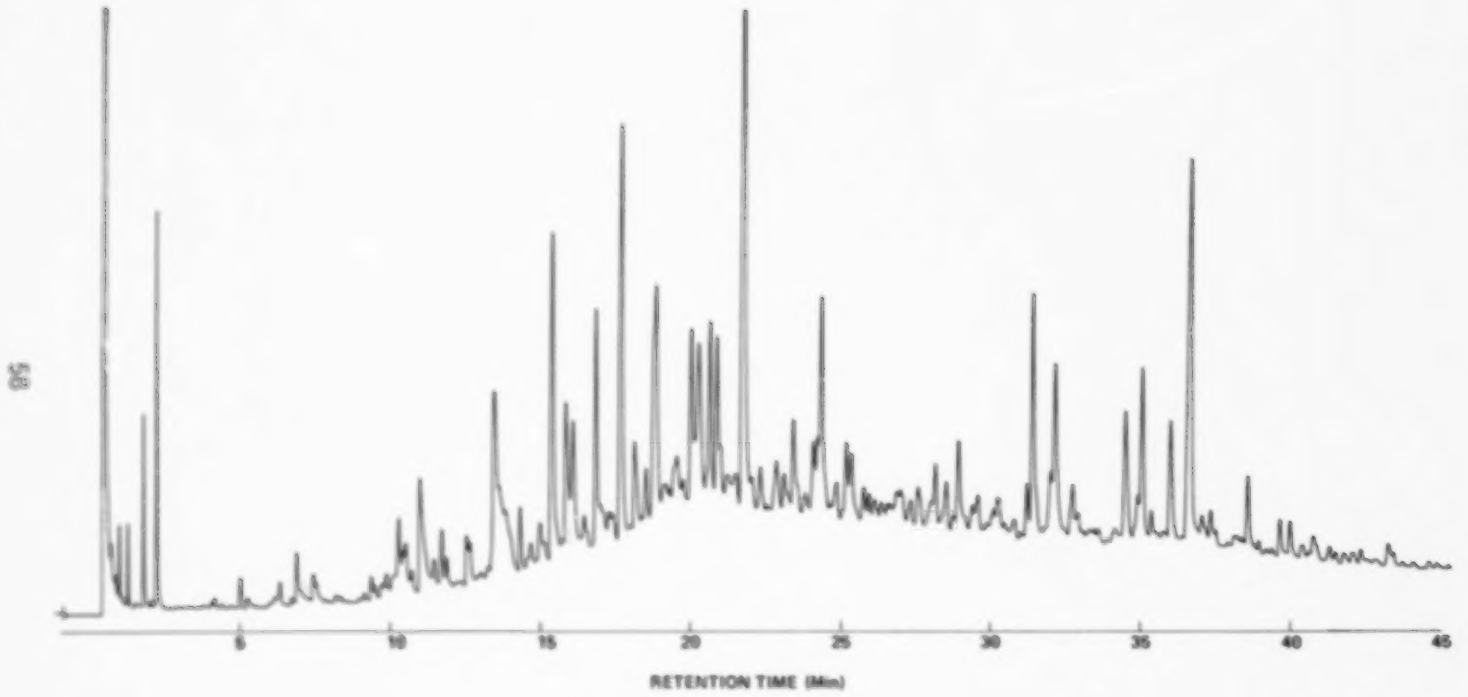


Figure 51. Capillary Gas Chromatogram of Vacuum Distilled Insoluble Oil Cut F-4.

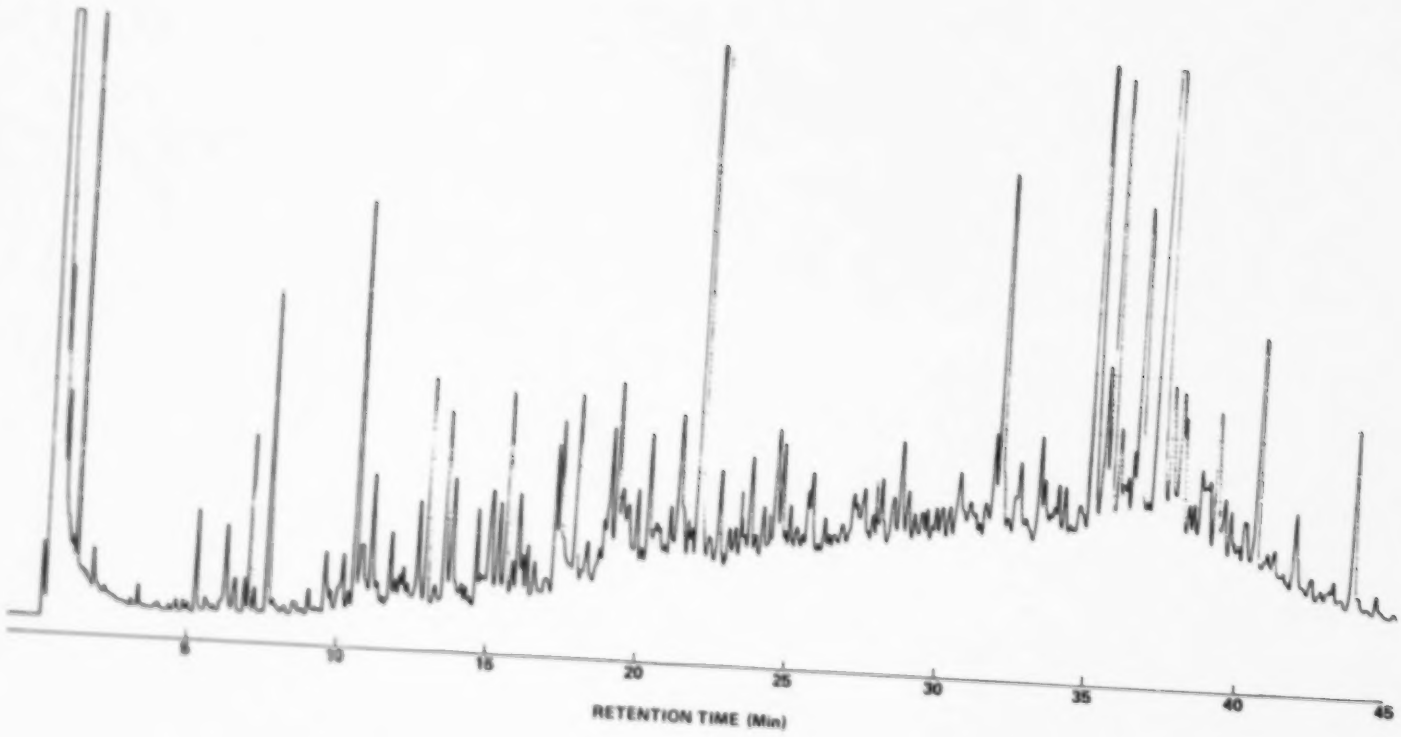


Figure 52. Capillary Gas Chromatogram of Vacuum Distilled Insoluble Oil Cut F-5 (B.P. 171-185°c/6mm).

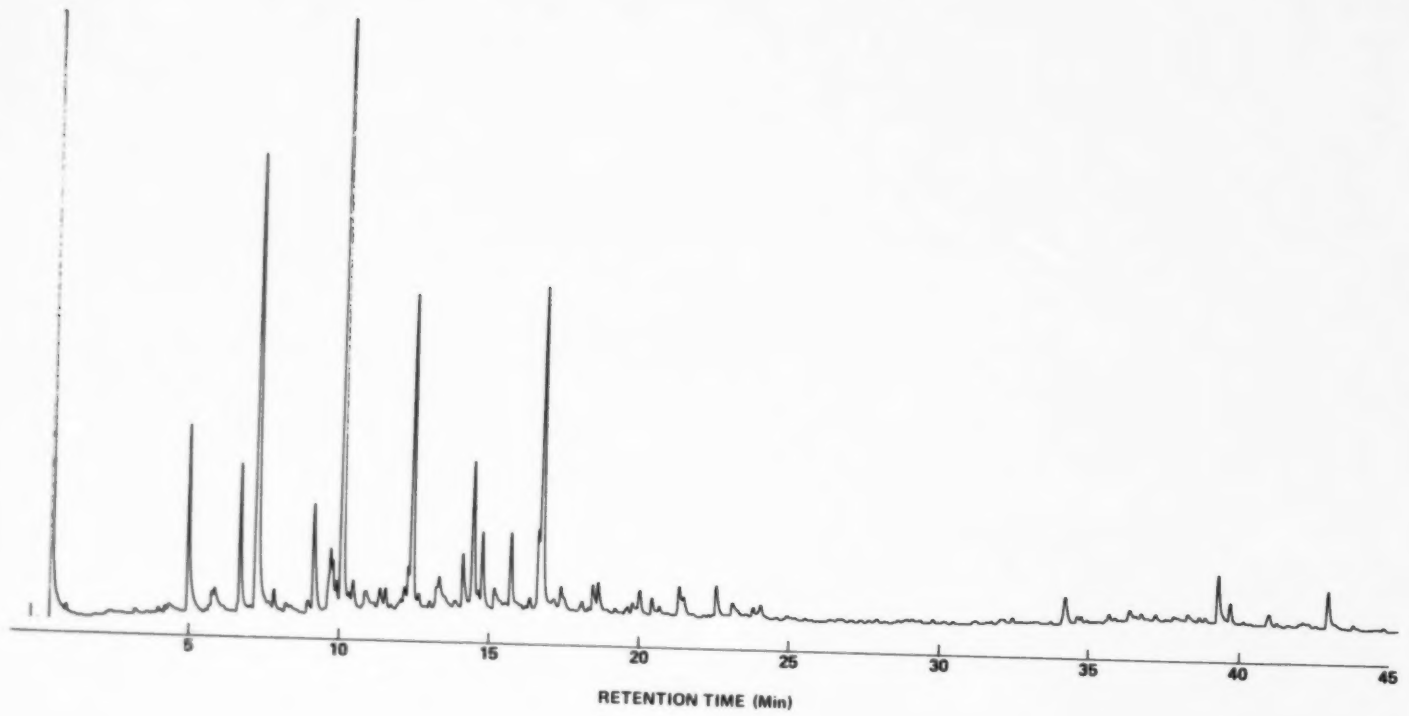


Figure 53. Capillary Gas Chromatogram of Insoluble Oil Fraction I-OR.

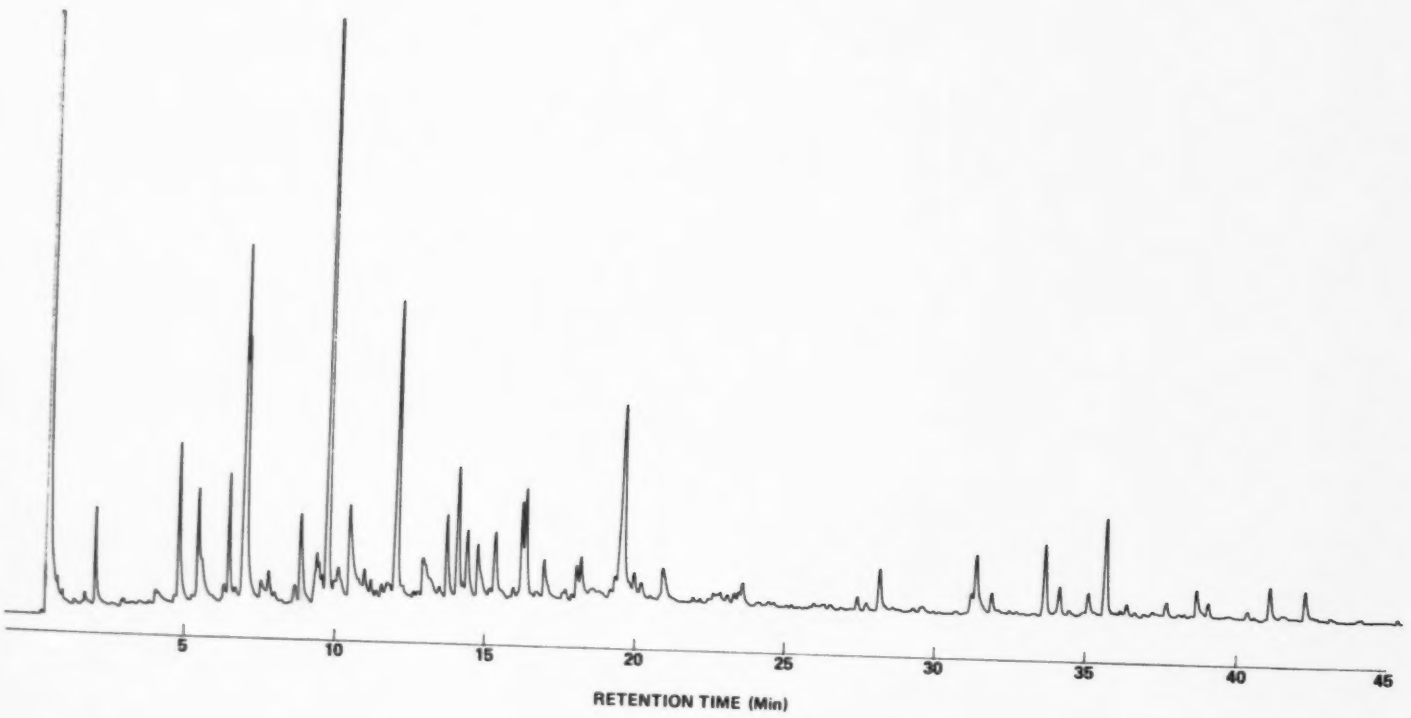


Figure 54. Capillary Gas Chromatogram of Insoluble Oil Fraction E-6.

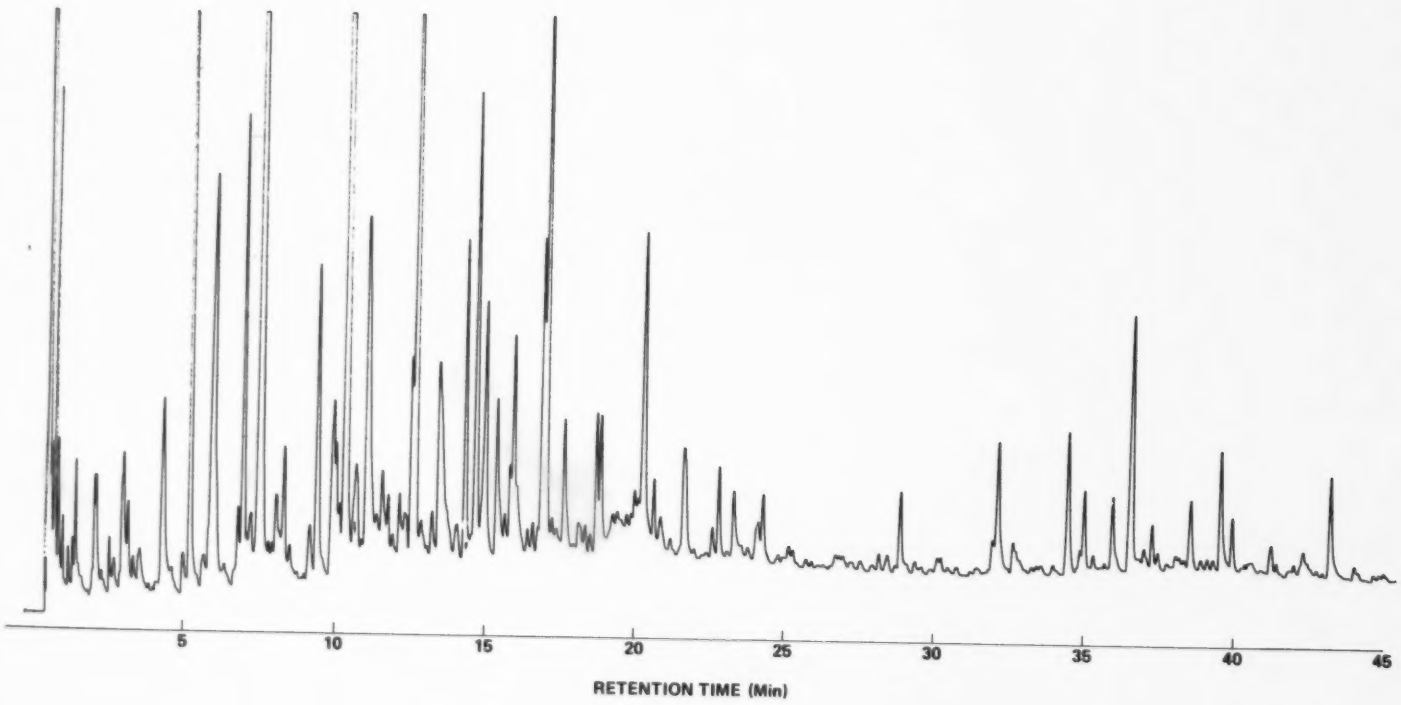


Figure 55. Capillary Gas Chromatogram of Insoluble Oil Fraction E-7.

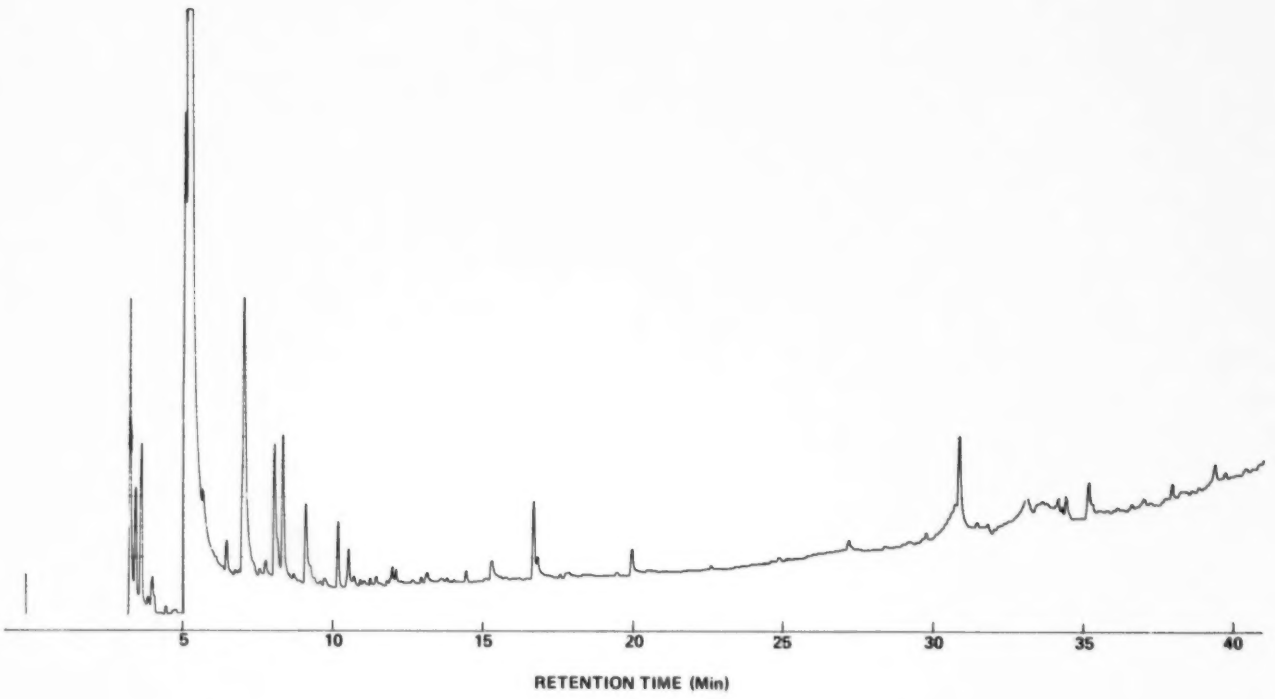


Figure 56. Capillary Gas Chromatogram of Volatile Fraction E-9.

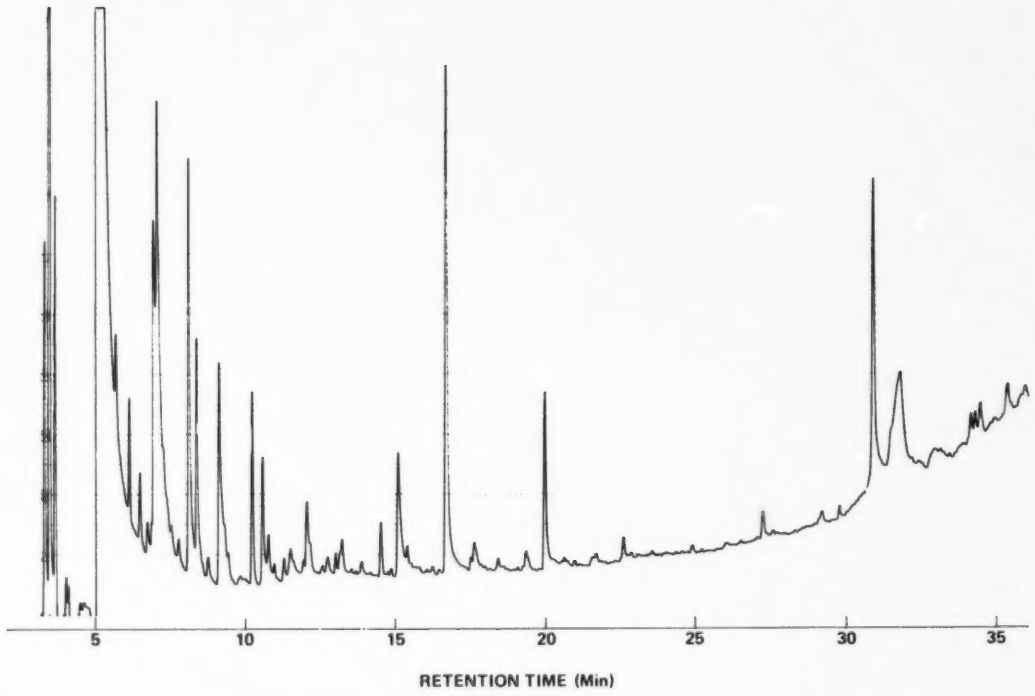


Figure 57. Capillary Gas Chromatogram of Volatile Fraction E-7.

TABLE 23. Results of Capillary Gas Chromatography of E-5 MiBK Fraction*

Retention Time (Min.)	Component
2.1	Furfural
5.0	Phenol
6.7	o-Cresol
7.3	Guaiacol
10.2	2-Methoxy-4-methylphenol
10.8	m-methoxyphenol
12.4	2-Methoxy-4-ethylphenol
14.5	Eugenol
14.8	2-Methoxy-4-propylphenol
15.8	Cis-Isoeugenol
16.8	trans-Isoeugenol

*Analysis performed on CP Sil-5 Column

TABLE 24. Results of Capillary Gas Chromatography for F-1, F-2, F-4, F-5, I-OR, E-6, and E-7 Insoluble Oils.*

Component	Sample and Retention Time (Min.)						
	F-1	F-2	F-4	F-5	I-OR	E-6	E-7
Furfural			2.2			2.0	2.0
Phenol	5.1	5.0		5.2	4.9	5.4	5.2
o-Cresol	6.8	6.7		7.0		6.9	6.9
Guaiacol	7.4			7.6	7.2	7.0	7.5
2-Methoxy-4-methylphenol	10.3	10.1	11.0	10.6	10.1	10.4	10.4
m-Methoxyphenol		10.9					11.0
2-Methoxy-4-ethylphenol		12.4				12.0	12.6
Eugenol	14.6	14.3	15.4	15.0	14.4	14.4	14.7
2-Methoxy-4-propylphenol	15.0	14.5		15.6	14.7		15.0
cis-Isoeugenol	15.9	15.7	16.8		15.7	16.2	15.9
trans-Isoeugenol		16.8	17.7		16.7	16.9	17.0

*Analysis performed on CP Sil-5 Column

TABLE 25. Results of Capillary Gas Chromatography of E-6 and E-7 Volatiles.*

Component	Sample and Retention Time (Min) E-6	E-7
Acetic Acid	5.2	5.2
Furfural	8.3	
Phenol		15.1
Guaiacol	16.7	16.7
2-Methoxy-4-methylphenol	20.0	20.0

*Analysis performed on an SP-2100 Column

GS-Mass Spectrometry of Extraction Samples*

Volatiles

The gc-ms total ion current chromatograph of E-6 volatiles is shown in Figure 58. The assignments are as follows:

Scan Number	Assignment
4	acetic acid
19	a butanol
29	a pentanol
33	a pentanol
40	furfural
55	o-cresol
78	a cresol
95	a cresol
104	Guaiacol
133	2-methoxy-4-methylphenol

The gc-ms total ion current chromatogram of E-7 volatiles is shown in Figure 59. The assignments are as follows:

Scan Number	Assignment
6	acetone
23	acetic acid
40	a butanol
59	a pentanol
79	furfural, furfuryl alcohol
87	a pentanol
104	a heptanol
135	a heptanol
152	a heptanol
163	o-cresol
182	Guaiacol
224	2-methoxy-4-methylphenol

Insoluble Oils

The total ion current chromatogram of E-6 insoluble oil is shown in Figure 60. The assignments are as follows:

Scan Number	Assignments
8	acetone
76	furfural
101	phenol
122	o-cresol
129	a cresol
140	Guaiacol
164	2-methoxy-4-methylphenol
186	2-methoxy-4-ethylphenol
207	2-methoxy-4-propylphenol
220	Isoeugenol
229	Isoeugenol

The total ion current chromatogram of E-7 insoluble oil is shown in Figure 61. The assignments are as follows:

Scan Number	Assignments
66	furfural
107	o-cresol
122	phenol
143	a cresol
160	a cresol
178	unknown (mw 112)
188	Guaiacol
205	unknown (mw 122)
222	Veratrole
234	2-methoxy-4-methylphenol
266	2-methoxy-4-ethylphenol
301	Isoeugenol and 2-methoxy-4-propylphenol

The total ion current chromatogram of F-1 is shown in Figure 62. The assignments are as follows:

Scan Number	Assignments
108	phenol
125	o-cresol
145	m- or p-cresol
159	m- or p-cresol
172	Guaiacol
203	2-methoxy-4-methylphenol
258	Isoeugenol

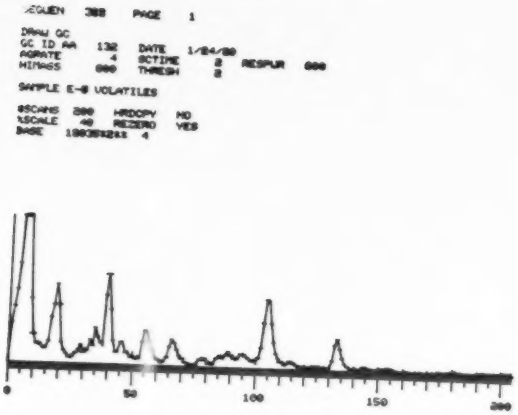


Figure 58. Reconstructed Gas Chromatogram of Volatile Fraction E-6.

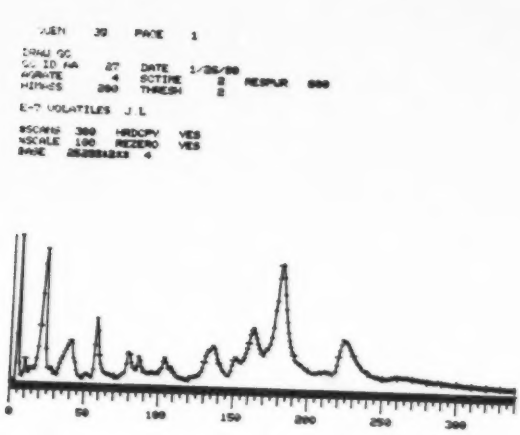


Figure 59. Reconstructed Gas Chromatogram of Volatile Fraction E-7.

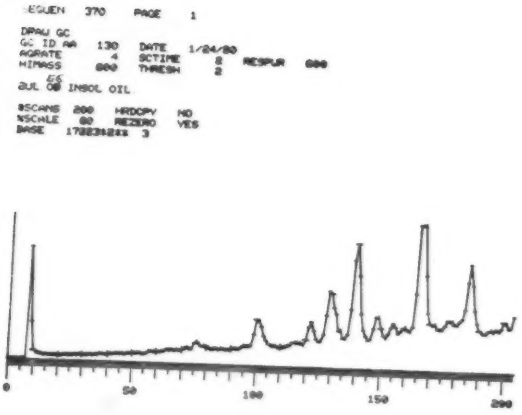


Figure 60. Reconstructed Gas Chromatogram of Insoluble Oil Fraction E-6.

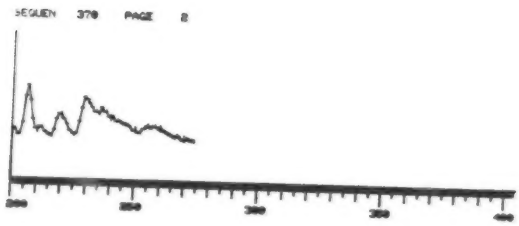


Figure 60 cont. Reconstructed Gas Chromatogram of Insoluble Oil Fraction E-6.

The total ion current chromatogram of F-2 is shown in Figure 63. The assignments are as follows:

Scan Number	Assignments
93	Phenol
113	o-cresol
127	m- or p-cresol
133	m- or p-cresol
153	Guaiacol
192	Veratrole
206	2-methoxy-4-methylphenol
250	unknown

MiBk Extracts

The total ion current chromatogram of E-5 MiBK is shown in Figure 64. The assignments are as follows:

Scan Number	Assignments
80	furfural
115	o-cresol
132	m- or p-cresol
145	Guaiacol
163	unknown (mw 132)
180	unknown
195	2-methoxy-4-methylphenol
232	2-methoxy-4-ethylphenol
275	Eugenol and/or Isoeugenol

The total ion current chromatogram of E-6 MiBK is shown in Figure 65. The assignments are as follows:

Scan Number	Assignments
3	acetone
89	phenol
109	o-cresol
116	m- and/or p-cresol
124	Guaiacol
137	Veratrole
149	2-methoxy-4-methylphenol
154	unknown (mw 112)
169	2-methoxy-4-propylphenol
183	Eugenol
202	Isoeugenol

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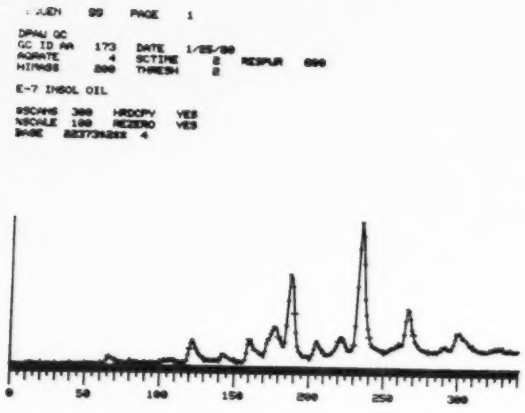
SEQUEN 99 PAGE 1
DRAW QC
GC ID AA 173 DATE 1/25/80
AQRATE 4 SCTIME 0 RESPLR 600
HIMASS 200 THRESH 0
E-7 INSOL OIL
0 50 100 150 200 250 300

Figure 61. Reconstructed Gas Chromatogram of Insoluble Oil Fraction E-7.

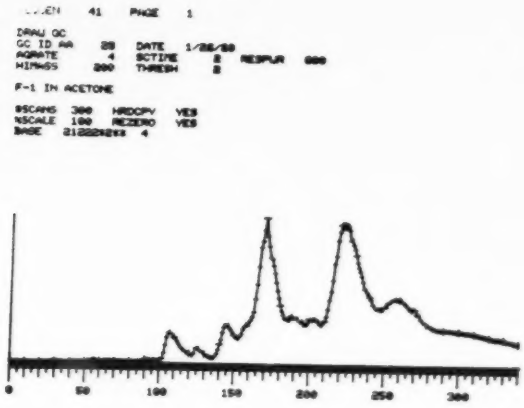
SEQUEN 41 PAGE 1
DRAW QC
GC ID AA 88 DATE 1/26/80
AQRATE 4 SCTIME 0 RESPLR 600
HIMASS 200 THRESH 0
F-1 IN ACETONE
0 50 100 150 200 250 300

Figure 62. Reconstructed Gas Chromatogram of Vacuum Distilled Insoluble Oil Cut F-1.

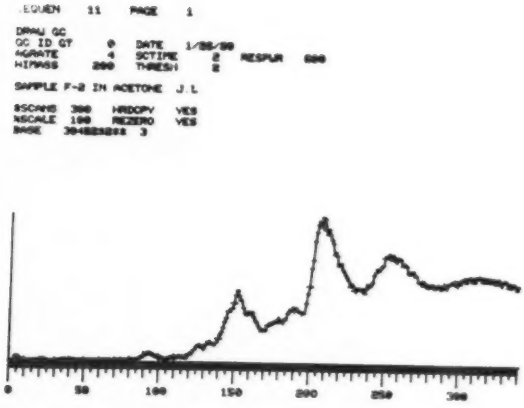
SEQUEN 11 PAGE 1
DRAW QC
GC ID GT 0 DATE 1/25/80
AQRATE 4 SCTIME 0 RESPLR 600
HIMASS 200 THRESH 0
SAMPLE F-2 IN ACETONE J L
0 50 100 150 200 250 300

Figure 63. Reconstructed Gas Chromatogram of Vacuum Distilled Insoluble Oil Cut F-2.

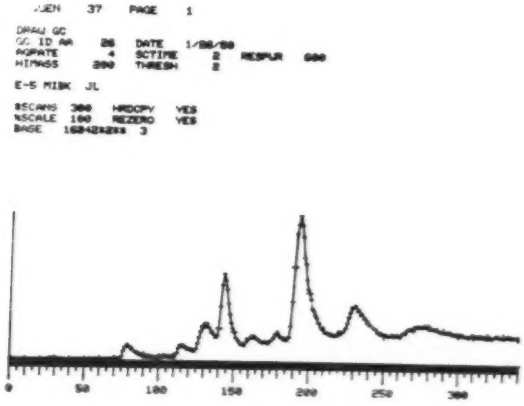
SEQUEN 37 PAGE 1
DRAW QC
GC ID AA 86 DATE 1/26/80
AQRATE 4 SCTIME 0 RESPLR 600
HIMASS 200 THRESH 0
E-5 MIBK JL
0 50 100 150 200 250 300

Figure 64. Reconstructed Gas Chromatogram of E-5 MIBK Extract.

The total ion current chromatogram of G-7 WiDE is shown in Figure 66. The assignments are as follows:

Scan Number	Assignments
38	furfural, furfuryl alcohol
63	a hexanol and a heptanol
83	phenol
100	o-cresol
121	m- and/or p-cresol
147	Guaiacol
160	naphthalene
176	Veratrole
192	2-methoxy-4-methylphenol
226	2-methoxy-4-propylphenol

The total ion current chromatogram of G-8 WiDE is shown in Figure 67. The assignments are as follows:

Scan Number	Assignments
83	Phenol
119	o-cresol
137	m- or p-cresol and unknown (mw 112)
160	Guaiacol
183	unknown (mw 112)
196	2-methoxy-4-methylphenol
218	2-methoxy-4-ethylphenol
244	Eugenol and/or Isoeugenol

*These gc-ms runs were made under the following conditions: Column - 6 ft x 1/8 in., OV-17 stainless steel, Flow rate to 30 ml/min; Initial Temperature 60°C; Final Temperature 280°C; Programming Rate, 6°C per min.; Detector - Flame Ionization.

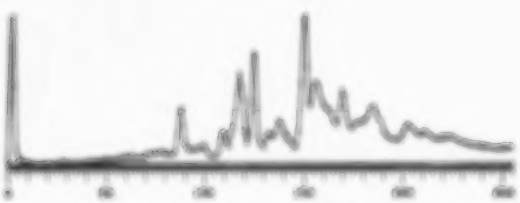

Figure 65. Reconstructed Gas Chromatogram of B-6 HIBK Extract.

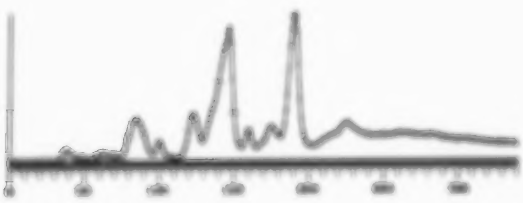

Figure 66. Reconstructed Gas Chromatogram of B-7 HIBK Extract.

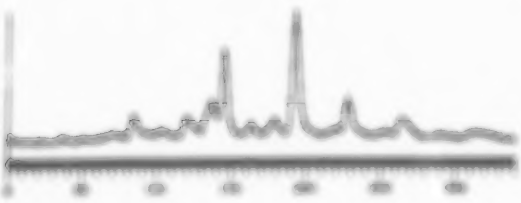

Figure 67. Reconstructed Gas Chromatogram of B-8 HIBK Extract.

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